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# SPACE SCIENCE APPLICATIONS OF SOLID STATE LUMINESCENCE PHENOMENA

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SPACE APPLICATIONS OF SOLID STATE  
LUMINESCENT PHENOMENA

Proceedings of a workshop organized by the

**MATERIALS RESEARCH LABORATORY**

The Pennsylvania State University  
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## INTRODUCTION

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This "workshop," the proceedings of which are reported in this collection, was one in a series held by the Materials Research Laboratory. Our effort in such meetings is to create an atmosphere more or less the opposite of a national meeting. Such workshops are held exclusively for scientists, actively working in some well defined field, who would normally not interact with each other because they have different disciplinary backgrounds and belong (typically) to different scientific societies. Hence in this workshop are represented astronomers, mineralogists, geochemists, geophysicists, and solid state physicists, all concerned with luminescence phenomena associated with the materials likely to be present in near space bodies.

These conclusions emerged from our discussions extending over the two days:

1. It is clear that the close cooperation of mineralogists and physicists is essential for conducting the best research, and avoiding some obvious errors, on luminescent phenomena of natural materials. While such a conclusion might appear to be so obvious as to be banal, it would appear to be a worthwhile recommendation as a pre-condition for future research.
2. It became clear during the course of the discussions that no ordinarily involved mechanism of "luminescence" could possibly explain the intensity or the geographic distribution of the transient luminescent phenomena observed on the moon (and the galactic cloud). There appeared to be no doubt either about the reality of some of the observations, nor any about their transience and connection with some type of solar activity. Yet no known photoluminescence (excited by u-v, x-rays or the particulate radiation in the solar wind), triboluminescence, or thermoluminescence phenomena appear to offer any hope as an explanation. The chemically-pumped luminescence, newly-reported by the host institution, is worthy



of further study as a mechanism but is no more than one more possibility at this stage.

3. The major item which the assembled group agreed to recommend as a proposal to the appropriate international space agencies concerned the need for a coordinated international fully instrumented equivalent of the "Moon Blink" program to attempt to settle unequivocally the existence, location, and quantitative parameters of transient luminescent phenomena. Such a program would provide at relatively low cost definitive insight into a phenomenon, which--as seen from the above--remains a major observed and unsolved puzzle in the behavior of solid matter in the space environment. It would continue on international cooperation in space research begun in IGY and IYQS.



## LUMINESCENT PHENOMENA ON THE MOON AND IN INTERPLANETARY SPACE

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It is well known that, in the visible spectral domain, the light of the Moon constitutes essentially sunlight multiply scattered from the lunar surface in a way which leaves its spectral composition largely unchanged. The surface of the Moon is, however, on the whole a very poor reflector: on average, only about seven per cent of incident sunlight gets back-scattered by it in all directions. The most part of it gets absorbed and re-emitted in the infra-red wavelengths to which our atmosphere is but partly transparent through two or three discrete windows. On the whole, for wavelengths shorter than  $1\mu$ , the light of the lunar surface (or of the solid surface of Mercury, Mars, of the zodiacal cloud) is dominated by scattered sunlight; while the radiation at wavelengths in excess of  $1\mu$  is due to thermal emission of the respective bodies.

The question can, however, be asked: does scattered sunlight, together with that absorbed and re-emitted by the lunar or solid planetary surfaces at generally lower frequencies represent the total radiation we receive from these bodies? Indications of additional sources of emission which may, at times, make an appreciable contribution to the total light of these bodies--and, in particular, to that of the Moon--have been forthcoming from different directions for many years; and the aim of the present paper will be to give a brief account of the relevant observational facts as well as of their tentative interpretation.

To begin with the most elementary manifestations which may be associated with an additional source of light, it has been noted by many observers in the past (cf. e. g. Rougier, 1933) that the apparent brightness of the Moon at a given phase (when due regard is paid to reductions in its instantaneous distance from the Earth, libration, etc.) is not quite the same from year to year; and these fluctuations appear to be correlated with the cycle of solar activity (though their amplitude seemed larger than that manifested by the solar constant). According to the most recent photometric studies by Gehrels and his associates (cf. Gehrels et al., 1964), between 1956-59 (i.e., near the



maximum of the last cycle of solar activity) the lunar surface was between 10-20 per cent brighter in visible light than between 1963 November - 1964 January, when solar activity was near its minimum. Moreover, a recent analysis by Hopmann (1965) of numerous individual photoelectric observations of the Moon by Wildey and Pohn (1964) revealed the existence of numerous measurements of increased brightness (comparable with those noted by Gehrels) which exceeded by far the limits of observational errors.

Similar results have also been obtained by van Diggelen (1964) and, more recently, by Koomen, Tousey and Seal (1969) who succeeded in photographing the Earthshine on the Moon at a phase of only  $1^{\circ}.2$  away from "new" with the aid of a rocket-borne coronagraph on 9 May 1967. According to these investigations, the features of the earth-lit Moon (in particular, the lunar bright rays on mare background) showed greater contrast at "new" than at "full" Moon--a fact suggesting that, under direct sunlight, brightness contrasts are lessened by differential fluorescence of solid surface.

Another indication of solar influence on global brightness of lunar eclipses was brought to light first by Danjon (1920), by a discussion of the data extending over 3-1/2 centuries. Danjon proved that the brightness of the eclipsed Moon was strongly correlated with the cycle of solar activity; its residual light at the time of totality was found to increase with advancing cycle, and to drop abruptly at the time of the minimum of solar activity, in such a way that eclipses just preceding a minimum of solar activity are brighter than those following it. One other feature comes to mind which also changes abruptly at the minimum of solar activity: namely, the location of sunspots and associated disturbed areas on the apparent solar disk, which are known to expire near the equator at the end of a cycle to re-appear in high latitudes at the commencement of the next one. Since 1920, Danjon's evidence was supplemented by De Vaucouleurs (1944) on the basis of 47 eclipses observed between 1893-1943; and further confirmed by Link (1963) or Bell and Wolbach (1965).

Evidence of solar influences producing anomalous photometric effects during lunar eclipses is not limited only to fluctuations in total brightness of the eclipsed Moon, but extend also to the partial phases. Photometric studies by Link (1946) and others (Cimino and Fortini, 1953; Cimino and Fresa, 1958) of partial phases of lunar eclipses, during which the loss of light was found to be less than that expected from the geometry of the Sun-Earth disks--indicated that significant effects are being produced by illumination of the

Moon by uneclipsed parts of the solar corona. The latter emits but negligible fraction of visible light, but (on account of its high temperature) a much larger proportion of x-rays; and Link conjectured that this hard radiation produces luminescence on the lunar surface accounting for the anomaly. On the other hand, Matsushima (1966) asserts the existence of a positive correlation between the residual eclipse brightness and the index  $K_p$  of geomagnetic activity--which, in turn, is correlated with the solar wind flux rather than sunspot activity.

There exists, furthermore, another way in which the luminescence of the lunar surface could be established from observations of integrated light: namely, by measures of polarization anomalies of moonlight (and of their dependence--if any--on the wavelength). The basic idea goes back to the fact that, whereas the fraction of the moonlight which represents scattered sunlight becomes polarized by this process--and the degree as well as the position of the plane of polarization varies with the phase--the luminescent emission would, of course, be non-polarized. Therefore, any temporary anomalies on the phase-polarization curves which exceed the limits of observational errors--manifested so clearly on Lyot's excellent measurements (Lyot, 1929)--may (as we recently pointed out by Gehrels) have been caused by variable admixture of non-polarized light of luminescent origin. Moreover, the polarization of scattered moonlight is known to vary but slowly with the wavelength. Therefore, any irregularities on the curve of polarization versus wavelength should indicate--no less distinctly than the filling-up of the absorption lines of the lunar spectrum--the presence of luminescent bands at the respective frequency (Teyfel, 1960).

Photometric or polarimetric studies of the global (or local) integrated light of the Moon, referred to above, have thus provided clear indications of the fact that the Moon exhibits (at least at times) the presence of additional source of light which is independent of scattering or thermal emission. It suggested, moreover, the existence of some relationship between these optical phenomena and solar activity. However, these observations could reveal but little about the spectral composition of this additional light of luminescent origin. In order to learn more about it, it becomes necessary to resort to spectrophotometric methods of investigation; and this has so far been done mainly by the so-called "line-depth method" (based on the observed filling-up of the cores of absorption lines of the lunar spectrum relative to their wings by additional light of luminescent (or other) origin, in contrast with the



original profile of the same line in parent sunlight.

This "method of line depths" for a determination of the fractional luminescence of the lunar surface was proposed originally by Link (1951) and employed in practice first by Kozyrev (1956) and Dubois (1957, 1959) using photographic techniques. Photoelectric spectrometry of this type was performed first by Grainger and Ring (1962); and later by Spinrad (1964), Wildey (1964), Scarfe (1965), Myronova (1965), Ney et al. (1966), McCord (1967) and others.

The results of their work disclosed, first, that the lunar luminous phenomena, presumably of luminescent origin, are transient in time; for they do not always occur in the same place with the same amplitude. The latter were found to oscillate between zero and more than 30% of the brightness of the adjacent continuum--mostly (though not exclusively) in the light of the H-line of CaII (particularly suitable for this work by virtue of its great depth as well as position in the spectrum). McCord (1967) observed mostly amplitudes ranging between 0.5-5%; while Kozyrev (1956) or Dubois (1957, 1959) recorded somewhat larger effects--mostly in the light of the H-line of CaII (particularly suitable for work of this type on account of its great depth and position in the spectrum). Grainger and Ring (1962) or Spinrad (1964) reported occasionally effects exceeding 10% in amplitude; while Scarfe (1965) recorded, in a group of FeI lines near  $\lambda 5450\text{\AA}$ , transient luminous events attaining an intensity as high as 30% of the adjacent continuum on 5 October 1963--while in H $\alpha$  or the sodium D-lines no effects exceeding 2% could be detected at the same time. As far as regional dependence is concerned, the crater Aristarchus showed the strongest effect, but Copernicus almost as strong; and Kepler only somewhat less. On the other hand, Wildey (1964) or Ney and his associates (Ney et al., 1966) failed to detect any spectral effect attributable to luminescence with their instruments, by the line-depth method, at the time of their observations.

Lastly, one additional and highly interesting result should be pointed out in this connection; and the first one obtained by an experiment aboard a lunar spacecraft. The Russian probe Zond 3 during its lunar fly-by on 20 July 1965 obtained sequentially 14 spectrograms of the Moon in the domain between 1900-2750 $\text{\AA}$  (with 14 $\text{\AA}$  spectral resolution)--i.e., in far ultraviolet which does not penetrate through the atmospheric ozone. At the time of observation, the field of view of the spectrometer was about 3°, subtending on the lunar surface an area close to 500 km across; hence, each scan analyzed light averaged over

about one-quarter of the apparent lunar disc (mainly continental areas on the far side). An analysis of these spectra disclosed (among others) one interesting fact: namely, a conspicuous enhancement of intensity between  $2420\text{--}2720\text{\AA}$ , shown on all spectra but fluctuating in time between 10-50 per cent of the intensity of adjacent continuum. Lebedinsky et al. (1967 a,b) tentatively ascribed this phenomenon again to luminescence of the lunar surface under fluctuating external influences; and pointed out that, inasmuch as their scans averaged light over large areas of the Moon, the actual luminescence--if localized--could have been very much more intense.

Are any of the transient luminous phenomena on the Moon, reported so far by the spectroscopists, intense enough to be observable with devices of lower spectral resolution (such as filters) or with the naked eye? This appears indeed to have been the case, and repeatedly so; as is attested by many reports of the past--among which the lunar events described by William Herschel in 1787 (cf. Kopal, 1969) or Edward Emerson Barnard (cf. Hopmann, 1967) deserve particular attention. Moreover, twice in the past decade conspicuous transient luminous phenomena were recorded on the Moon within a few weeks of each other. The first instance occurred on 30 October 1963, when Greenacre and Barr (Greenacre, 1963) at Lowell Observatory noted that three distinct spots in the neighbourhood of the crater Aristarchus flared up temporarily in reddish light, intensively enough to be visible without the aid of any filter. The phenomenon lasted about 25 minutes; and its intensity seemed to fluctuate during this time.

Less than three days later (but before anything was known about the Lowell results in Europe), Kopal and Rackham (1963) working at the Observatoire du Pic-du-Midi, succeeded in taking the first photographs of another--and by area much larger--"lunar flare" during the night of November 1-2, 1963 in the region of Oceanus Procellarum around the crater Kepler. Photographs taken with the Observatory's 24-inch refractor through an interference filter centered at  $\lambda 6725\text{\AA}$  showed conspicuous brightening (by as much as 82%) of the region covering some  $60,000\text{ km}^2$  of lunar ground which recurred twice that night--each time lasting no more than 15-20 minutes; while control photographs taken at the same time through a green filter (centered on  $\lambda 5450\text{\AA}$ ) showed nothing unusual. These transient enhancements in the red constitute the largest (though not necessarily most intense) phenomena of this kind recorded so far; and together with the visual observations at Lowell represent the best evidence of a rapid time variation of these phenomena.



Since 1963, a search for transient colour changes on the Moon has been continued photographically by Rackham (1967) and photoelectrically by Roberts (1966, 1969). This latter investigator employed a three-colour photoelectric photometer of beam-splitting type, capable of simultaneous registration of light intensities through three different channels (centered at  $\lambda\lambda 5400, 5700$  and  $7900\text{\AA}$ ). Extensive use of this equipment in the past three years led to a confirmation that transient changes reaching up to 0.2 magn. in colour occur frequently in the marial regions on the Moon (in particular, in Oceanus Procellarum between the craters Copernicus, Kepler and Aristarchus). They appear to be strongly localized, and transient on the time-scale of minutes, (some changes occurring within less than one minute have been recorded, which could be of neither atmospheric, nor instrumental origin). It has, however, been so far impossible to associate such phenomena unambiguously with any particular type of lunar ground; nor the times of their occurrence with any non-lunar event has as yet been established. Possible correlation between the lunar transient colour changes and the interplanetary magnetic index  $K_p$  seems again indicated (cf. Foukal, 1968); but more extensive material than that so far available will be needed to place such a correlation on a more secure empirical basis.

In order to secure such a basis with the aid of observations which can be more readily made, and are less time-consuming than impersonal photoelectric registration, an international programme of lunar visual colourimetry has been recently launched under the code name of Project MOONWATCH, monitored from NASA Goddard Space Flight Center (cf. Cameron, 1965) and reports of hundreds of transient lunar colour changes have been received from observers in many countries. Unfortunately, it is very difficult for such observations to attain the degree of objectivity as impersonal photoelectric work; and the data collected so far probably contain a mixture of chaff with wheat which are almost impossible to separate from each other; and the same is also true of past records of such events which left their echo in published literature. Thus Burley and Middlehurst (1966) compiled a chronological list of 238 transient phenomena on the Moon reported between 1587-1965; and an even longer list of over 550 such events was since collected by Cameron (1968). It is, however, difficult to assess at present the quality of each bit of such historical evidence with the requisite degree of criticism; and, for this reason, its analysis can lead at best to only tentative conclusions.

One event of this type deserves, however, an honourable mention in this place; for although it is based on visual observations, these observations were made in lunar proximity by the astronauts of Apollo 11 mission on 19-20 July 1969--a day before the first manned landing on the surface of our satellite. In particular, at 1845 GMT on 19 July the astronauts Armstrong, Aldrin and Collins reported to the NASA Manned Spacecraft Center at Houston unusual luminous activity on the walls of the crater Aristarchus--a phenomenon which was noted independently at the Dominion Astrophysical Observatory at Victoria, Canada (observers: Younger and Byl, using the Observatory's 48-inch reflector) and also in Borhum, Germany (observers: Pruss and Witte). Neither group of the terrestrial observers had any idea of the report of the astronauts at that time; but agreed in the time and place with them to a minute.

How to account for all these phenomena in terms of acceptable physical theory? Even if--to remain on safer ground--we restrict our attention only to recent events recorded by impersonal techniques, we are still faced with the following phenomena demanding explanation:

- (1) Brightness variations of sunlit Moon, apparently related with the 11-year solar cycle;
- (2) Changes in the degree of polarization of moonlight, apparently related with the same cycle;
- (3) Variations in the residual brightness of totally eclipsed Moon, correlated again with the 11-year solar cycle (and also, possibly, with the planetary magnetic index);
- (4) Local brightness variations on the face of sunlit Moon, evidenced by anomalous scatter in photoelectric observations of limited areas of the lunar surface;
- (5) Anomalous scatter in local polarization measures on many parts of the lunar surface; and
- (6) Transient variations in colour, observed visually or recorded photographically, spectroscopically, and photoelectrically over different parts of the lunar surface.

In the case of the diversity of these phenomena, it is indeed easier to say what cannot account for them; and in this way we can attempt to narrow down the field of admissible conjectures. First, let it be stressed that explanations in terms of ordinary thermal emission are out of the question, certainly for all transient events; for no known substance could possibly heat up (by whichever process) or cool down, to an extent which could make a



difference to visibility, in the time of minutes or even hours. Therefore, for reasons unknown at the time of William Herschel, the phenomena observed by him (and, later, by others) could have had nothing to do with volcanoes as we know them on the Earth. The anomalous emission of light on a time-scale indicated by the transient events must obviously be non-thermal--i.e., of luminescent origin, and confined to discrete bands of the spectrum.

Ordinary thermo-luminescence is, however, likewise ruled out by the fact that unexplained phenomena on the Moon do not follow the lunar thermal calendar; nor do they recur at any particular threshold of ground temperature. A possibility of photo-excitation of gas escaping from the lunar interior at the spots near Aristarchus exhibiting the anomalous colour phenomena was mentioned recently by Swings (1966) who conjectured that ammonia  $\text{NH}_3$  is dissociated by sunlight into  $\text{NH}_2$  and  $\text{H}_1$  and that the amine radical fluoresces in the red, as is observed, e.g., in comet tails. The quantitative consequences of such a hypothesis are, however, scarcely any more admissible; for too large a mass of gas would be required to account in this way for the luminous phenomena observed by Greenacre and Barr, and the discharge of such a mass of it into vacuum would be bound to bring about also structural changes of the surrounding landscape which have not been observed. The size of the Kepler enhancement as photographed by Kopal and Rackham makes these difficulties overwhelming; and the fact that such phenomena (particularly around Aristarchus) occur also at night-time--when no sunlight is available to cause photo-dissociation or luminescence--seems to rule out such a hypothesis altogether. For similar reasons, Opik (1967) concluded that the luminous phenomena observed in 1958 near the central mountain of the crater Alphonsus by Kozyrev (1962) were not due to fluorescence of escaping gas, but of solid ground.

The occurrence of transient events on the Moon is, we stress, uncorrelated with local temperatures on the Moon; and their origin must, therefore, be sought in outside influences. What else could, in turn, control external events more energetically than the Sun? The rhythm of the 11-year solar cycle is clearly making itself felt in lunar phenomena listed under (1)-(3) in the foregoing paragraphs; and it is only natural to ask to what extent more transient luminous phenomena ("lunar flares") may also be influenced by other specific aspects of solar activity?

Of these, the ones which immediately come to mind (because of a similarity of their time-scales) are solar flares. These are known to be as short-lived (from minutes to hours) as the observed lunar enhancements; and

while they last, they emit sufficient amount of energy--both electromagnetic (x-rays) and corpuscular (mainly protons)--to disturb the inner precincts of the solar system for hours and days afterwards. It is, in principle, quite simple to differentiate between the effects produced by their electromagnetic and corpuscular emission: for while the effects of x-ray emission--propagating with the speed of light--would reach the Moon at (virtually) the same time as the flare is observed on Earth, particles emitted from the flare may reach us with a time-lag of many hours (depending on their speed and directness of their trajectories).

It is interesting to note, in this connection--and this may, but need not, be a coincidence--that the appearance of the "red spots" near Aristarchus, as observed by Greenacre and Barr on October 30th, followed by 48 hours the Class 3 great solar flare of October 28th; and the Kopal-Rackham photographs of the enhancement of the Kepler region followed the same flare by 118 hours (and a Class 1 double flare of November 1st by 8-1/2 hours). Herschel's observations of the "volcanoes on the Moon" on April 18-19, 1787 coincided with a period of highly disturbed Sun, as was attested by the visibility in those days of polar aurorae in Europe as far south as Italy. On the other hand, the Greenacre-Barr observations of November 27th were made at a time when the Sun was exceptionally quiet.

Whatever the general case may be, one feature emerges from the foregoing facts quite clearly: namely, the none of the known transient lunar events occurred simultaneously with any major manifestation of solar activity; and could not, therefore, have been due to electromagnetic (x-ray) excitation. When we add to it the fact that, for instance, Herschel's "volcanoes" on the Moon of 1787 (as well as, according to Flamm and Lingenfelter (1965), the majority of the past lunar events) occurred on the dark (night) side of the Moon--which was cut off from direct sunlight at that time--the case against electromagnetic excitation becomes overwhelming; and the corpuscular radiation seems to offer the only remaining avenue of approach.

This road is feasible in principle; for not only can corpuscular radiation reach the Moon after a time-lag of the observed order of magnitude (i.e., from several hours to a few days), but particles of sufficient energy (spiralling along the respective lines of force) can impinge on any part of the day or night hemisphere of the Moon at any time, provided only that the gyro-radius  $\rho$  of such spirals exceeds that of our satellite. As is well known (c.f., e.g., Spitzer, 1954) this gyro-radius is given by the formula



$$\rho = \frac{E}{150H} \left( \frac{c}{v} \right) \text{ cm},$$

where  $E$  stands for the energy of the respective particles in electron-volts;  $H$  denotes the strength of the interplanetary magnetic field in gauss; and,  $v$  is the velocity of the moving particle, while  $c$  signifies that of light.

From extensive measurements performed in recent years by different types of spacecraft, the quantity  $H$  is known to fluctuate in lunar neighbourhood between  $5\gamma$  and  $50\gamma$ ; with a value of  $10\gamma = 10^{-4}$  gauss representing a fair average. If so, however, the radius  $\rho$  of gyration for (say) 10 keV protons proves to be approximately equal to  $1.45 \times 10^8$  cm, increasing to  $4.57 \times 10^8$  cm for 0.1 MeV protons, and  $1.45 \times 10^9$  cm for protons with energies of 1 MeV. Since the radius of the lunar globe is equal to  $1.738 \times 10^8$  cm, it follows that the radius  $\rho$  of proton gyration attains that of the Moon already for energies close to 11000 eV (corresponding to proton velocities of 1450 km/sec). Under average conditions prevailing in interplanetary space, protons with velocities in excess of 1500 km/sec can, therefore, impinge on the Moon anywhere and from any side; and such protons are known to form an important component of solar wind at the time of the disturbed Sun.

However, when we come to consider the quantitative aspects of the stimulation of lunar luminescence by corpuscular radiation, the situation becomes very much less satisfactory. The 1963 observations by Kopal and Rackham of the large enhancement of the Kepler region which temporarily almost doubled its surface brightness in the red indicated that the energy flux  $F$  of energy stimulating luminescent emission should have been of the order of  $10^5$  ergs/cm<sup>2</sup> (Kopal and Rackham, 1963, 1964); and for typical observations of luminescence by the "line-depth method" it could have been down to  $10^3$ - $10^4$  ergs/cm<sup>2</sup> sec. Now if protons alone had been responsible for its excitation, the energy balance would require that the ratio

$$\frac{F}{v} = \frac{1}{2} m_H v^2 N,$$

where  $m_H$  denotes the mass of a proton,  $v$  their velocity, and  $N$  their number per ccm. For  $m_H = 1.67 \times 10^{-24}$  g and  $F = 10^5$  ergs/cm<sup>2</sup> sec, the foregoing equation requires that the product  $Nv \sim 10^{29}$  sec<sup>-3</sup> for the 1963 November 1-2 events, and about  $10^{27}$  sec<sup>-3</sup> for small events observed spectroscopically through narrow passbands.

These numbers seem rather large. For  $v = 5000$  km/sec (about the maximum velocity of "slow" protons emitted by solar flares) the corresponding particle

density  $\underline{N}$  should be of the order of  $10^3 \text{ cm}^{-3}$  for the maximum flux of  $10^5 \text{ ergs/cm}^2 \text{ sec}$ , and 10-100 per ccm for more moderate events. Now the mean velocity of the quiet-Sun solar wind is known to be only about 400-500 km/sec; but the particle density  $\underline{N}$ , only about 0.1 per ccm. During storm conditions both the values of  $v$  and  $\underline{N}$  may increase, perhaps, ten times; but even this leaves us with values of  $\underline{N}$  which are about 100 times too small--a fact which discloses that such flux of corpuscular radiation as is known to be emitted by the Sun under all but perhaps the most abnormal conditions is insufficient for the excitation of transient events observed during lunar daytime.

If we turn our attention to the lunar night events--when luminescence has to compete in contrast only with Earthshine which is  $10^4$  times less intense than direct sunlight--luminescent glow concentrated in emission bands of 100-1000Å width and invoked by incident energy flux as low as 1-10  $\text{ergs/cm}^2 \text{ sec}$  could become visually observable. Only protons with energies in excess of 10 keV (i.e., velocities larger than 1500 km/sec) can, to be sure, follow interplanetary trajectories which are curved enough to enable them to impinge on the dark side of the Moon; but these are plentiful in space; so that any luminophor exposed to them on the lunar surface should become visible if the quantum efficiency of the light conversion process were one per cent or greater. Laboratory stimulation of proton-excited luminescence of common silicate rocks under ordinary temperatures indicated substantially smaller quantum efficiency of the process (cf., e.g., Nash, 1966, 1967); but subsequent work by Blair and Edgington (1968) has indicated that adequate efficiency can be obtained by the cooling of the samples to temperatures less than  $-100^\circ\text{C}$ , which prevail indeed on the lunar surface during most part of the night. Therefore, it is not difficult to account for the visibility of night-time luminescence on the Moon by the action of solar protons alone; but day time luminescence cannot be explained satisfactorily in this way; and its existence continues to confront us with a real problem.

The Moon is, incidentally, not the only astronomical body in space where we have encountered this problem. Another formation in which solid particles, probably of similar composition, are exposed to the entire range of solar energy output undiluted by any atmosphere is represented by the zodiacal cloud. And it is interesting to recall, in this connection, some events of the last solar cycle when, following the great flare (Class 3+) of 1958 July 7th, Blackwell and Ingham observed at Chacaltaya a temporary

reddening and general increase in brightness of the zodiacal light; and obtained evidence which satisfied them that the extra emission came from the interplanetary dust cloud. This phenomenon could again be scarcely understood otherwise than as luminescence produced by the corpuscular output of the flare (because of the time-lag of several hours between the solar event and the brightening of the cloud); but for an assumed particle density of 300 protons per ccm their velocity would have had to be in excess of 40000 km/sec to make the hypothetical luminescent process less than 100 per cent efficient.

This revealing (though so far unique) observation presents us with another example of a temporary enhancement (and reddening) of solid particles exposed to solar influences at a closer range than they are on the Moon; and its connection with the great flare of July 7, 1958 is--in this case--incontestable. Moreover, Blackwell and Ingham (1961) pointed out that the surface brightness of the zodiacal cloud at the time of their observations seemed also to be correlated with the planetary magnetic index  $K_p$ , and increased by as much as 40 per cent when  $K_p$  reached its maximum values between 7-8.

Of the other terrestrial planets in the solar system, Venus--like the Earth--is surrounded by an atmosphere which shields effectively its solid surface from any impact of solar corpuscular radiation (which produces the "auroal zones" in the upper atmosphere); and for Mars the Sun is too far for its radiation to produce any noticeable "auroal effects" in the atmosphere or on the ground. However, Mercury is much closer to the Sun than the Moon; and its surface is likewise unprotected by any atmosphere to speak of. It is, perhaps, relevant in this connection to recall that transient luminous phenomena--which may be similar to those on the Moon--have been reported for Mercury by Cruikshanks (1966); but again more data will be needed before possible analogy with the Moon can be pressed much further.

The complexity of all different phenomena reviewed in this paper, and the apparent difficulty to account for them in terms of an identifiable single process, leads us to conjecture that more than one process may be involved in giving rise to them. That the Sun is at the basis of them all, be their rhythm slow or fast, can be scarcely in doubt. However, the casual relationship between the solar and lunar phenomena is probably not simple, nor direct. One intermediary agent which can serve as a "go-between" in this connection may be the terrestrial magnetosphere, the tail of which can actually graze the Moon around the time of full-moon. The action of this

intermediary is suggested by correlations of some of the lunar (or zodiacal cloud) events with the magnetic index  $K_p$ . A possible relevance of this fact to lunar events has recently been emphasized by Cameron (1964), who pointed out that daytime luminescence as intense as that photographed by Kopal and Rackham on November 1-2, 1963 could have been caused, not by the direct impact of primary solar particles associated with a flare, but indirectly by their effect on the terrestrial magnetosphere. Thus the acceleration of solar protons in the geomagnetic tail may provide one way in which lunar transient events occurring in daylight (and, particularly, around the time of full-moon) could, perhaps, be accounted for by the solar wind of the observed intensity. Another way to do so would be open if the energy of the impinging corpuscular radiation could be temporarily stored in luminophors of suitable composition, to be available for release after a certain threshold charge has been built up, or by some more direct event acting as a trigger. But all these suggestions represent so far mere conjectures, to be quantitatively tested by subsequent investigations.

Summarizing the subject matter of the present paper we wish to stress, first, that transient luminous events--long indicated by several independent lines of observational evidence--should be regarded as recurrent phenomena, the reality of which is beyond doubt. Although the individual occurrences reported in this paper may have been subject to errors (observational, or instrumental) which are difficult to verify ex post in each instance, no conceivable combination of such errors could account for all events of this nature reported so far; the problem confronting us is merely to separate chaff from wheat--always a difficult one for phenomena of transient nature. Besides, transient luminous events with which we have been concerned in this paper do not apparently occur only on the Moon, but kindred phenomena have also been observed in zodiacal light (and on Mercury?)--i.e., whenever solid particles, unprotected by any atmosphere, are exposed to the full impact of solar radiation--both electromagnetic and corpuscular. In other words, the phenomena we are concerned with can scarcely be due to anything else but solid-state luminescence under conditions which we have been unable as yet to match properly in our own laboratories.

Astronomical observations carried out so far indicate, moreover, that such luminescence occurs preferentially in certain parts of the lunar surface, as though favouring a specific type of ground; and its spectrum does not appear to be continuous, but confined to emission bands at different



wavelengths (including ultraviolet). A transient emission of intensity amounting to a few per cent of that of the adjacent continuum in at least limited bandwidths seems, moreover, to be of fairly frequent occurrence. Instances of enhancement amounting to between 30 and 50 per cent (and possibly more) are on record; but their frequency can so far only be guessed at.

The establishment of a reliable correlation between the relevant solar events and their effects in other parts of the solar system will require many more observational data than those we now possess, and represents a goal for the future. However, from an obvious lack of simultaneous occurrence it is clear that luminescence on the Moon is not stimulated by solar electromagnetic (x-ray), but corpuscular, radiation which reaches the Moon after a transit time ranging from several hours to a few days. At daytime--in the absence of any appreciable magnetic field--particles of all energies can impinge on the lunar surface; while at night only more energetic particles ( $E > 10$  keV) can do so. Their numbers, as measured by independent experiments, are just about adequate to produce luminescence observable at night time, when their visibility has to compete in contrast only with earthshine; but for day time events the number of solar particles hitting the Moon directly seems deficient by at least two orders of magnitude; so that some secondary accelerating (or storage) facilities may have to be considered.

While astronomy and space physics can contribute to the solution of this important problem, its final solution must come from solid-state physics laboratories on the Earth; for the problem will not be really solved until we have identified the processes giving rise to lunar (and other cosmic) luminous transient phenomena, and matched them in the laboratory. Astronomy can furnish only circumstantial evidence from the sky that such phenomena exist, and demand explanation; but their proper explanation will ultimately rest with the solid-state physicist in the laboratory. Needless to say, the directness by which he can proceed to his goal will depend largely on the inspiration and guidelines provided by astronomical observational evidence. And the latter is as yet by no means complete--far from it! In point of fact, almost all that we know about luminescence on the Moon (and elsewhere in space) was learned by accident--when someone happened to be looking at the right place at the right time. While such accidental observations are sufficient for discoveries of the existence of new phenomena, they

are ill-suited to provide the documentation we need and a more secure guidance towards their explanation. Is this not a sufficient motivation for a systematic program of a more complete surveillance of the lunar face (as well as of the zodiacal light) by more accurate and impersonal methods than visual inspection to be initiated in the near future?

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THE LUMINESCENT AND THERMOLUMINESCENT PROPERTIES OF  
GRANITE AND ITS CONSTITUENT MINERALS AND THEIR  
RELEVANCE TO TRANSIENT LUNAR PHENOMENA

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Our previous luminescence studies on rocks and minerals (Blair and Edgington, 1968) had shown up some remarkable features for granite. These were: (i) a very large (approximately X 100) increase in the luminescent efficiency in the blue with reduction of temperature from +20°C to -196°C, and (ii) an intense red glow peak in the region of 0°C following irradiation at -196°C. We showed that this latter property might be relevant to transient lunar phenomena (Middlehurst *et al.*, 1968) as it provided a credible energy storage mechanism. Our previous work included the study of seven different granites, and we found that these properties were, to a greater or lesser extent, common to all of them. This led us to believe that these properties were associated with the major mineral constituents (feldspar, quartz and mica). We therefore thought it worthwhile to separate these minerals from a granite specimen and study their luminescent and thermoluminescent properties individually.

The granite chosen for this work was a microgranite from Duffton, Westmorland, England. It was suitable because of its coarse-grained nature which made manual separation of the constituent minerals fairly easy. The mica was in the form of muscovite. The feldspar was a pink, sodium rich, plagioclase whose composition lay near the albite end of the albite-anorthite isomorphous series.

Using the technique previously described (Blair and Edgington, 1968) we studied the luminescent and thermoluminescent properties of the separated mineral phases and compared them with those of the unseparated parent granite. The irradiation was done in the 160 MeV proton beam from the Harwell synchrocyclotron. Luminescent spectra were measured at +20°C and -196°C, and



the thermoluminescent glow curve in the wavelength band 6700 Å to 7500 Å following irradiation at  $-196^{\circ}\text{C}$  was recorded.

Figure 1 shows the spectra obtained at  $+20^{\circ}\text{C}$ . The data are normalised to a proton flux of  $3.88 \times 10^8$  per second, and the ordinate is the photomultiplier output current corrected for the variation of spectral response of the apparatus. We note that the spectra obtained for the granite and all the constituent minerals are very similar, showing an enhancement towards the red end of the spectrum, characteristic of many terrestrial, meteoritic and lunar minerals. Figure 2 shows the spectra obtained at  $-196^{\circ}\text{C}$ . We note that response from the feldspar is very similar to that from the parent granite, and that the quartz shows a dramatic increase in luminescent efficiency in the blue with respect to its value at  $+20^{\circ}\text{C}$ . We conclude that the large increase in efficiency in the blue with reduction of temperature seen in many granites, though not strikingly apparent in this one, is due to the constituent quartz. One should bear in mind that it is not always possible to make a quantitative comparison between the summed luminescent response of the constituent minerals, scaled by their relative abundances, with that of the parent, because one does not know to what extent the more luminescent minerals are masked by those which are less so.

Figures 3 and 4 show the thermoluminescence glow curves for the parent granite and constituent minerals respectively. These data have been normalised to an incident dose of  $6.34 \times 10^{11}$  protons and a heating rate of  $30^{\circ}\text{C}$  per minute. The ordinate gives the total rate of light output within the accepted wavelength band expressed in terms of electron volts per second. We note the striking similarity between the glow curves for the granite and the feldspar, compared to the small effects observed for the quartz and mica constituents. The difference between the peak temperatures of the two glow curves is explicable in terms of the different actual heating rates used during the two runs. The integrated light output from the two curves comes out to be equal to within 0.2%, which is well within the experimental uncertainties estimated at a few per cent. This integral has the value of  $2.12 \times 10^{12}$  eV. Assuming a rate of energy loss in the sample of  $4.25 \text{ MeV/gm/cm}^2$  per proton, and an optical depth of  $10 \text{ mgm/cm}^2$ , this yields a thermoluminescence energy efficiency of  $0.79 \times 10^{-4}$ . We conclude that it is the feldspar constituent that is responsible for the observed thermoluminescent properties of granite.

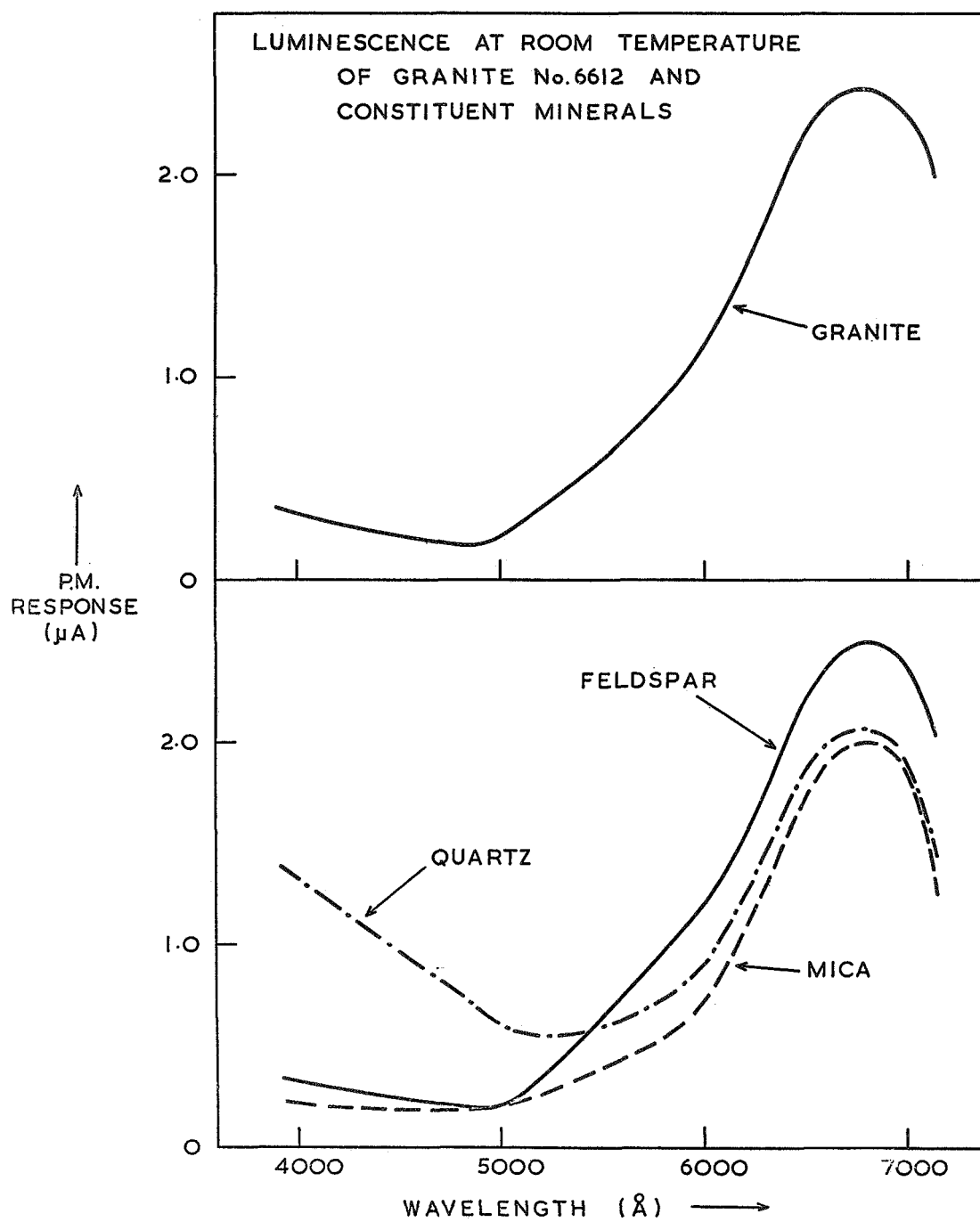


Fig. 1.

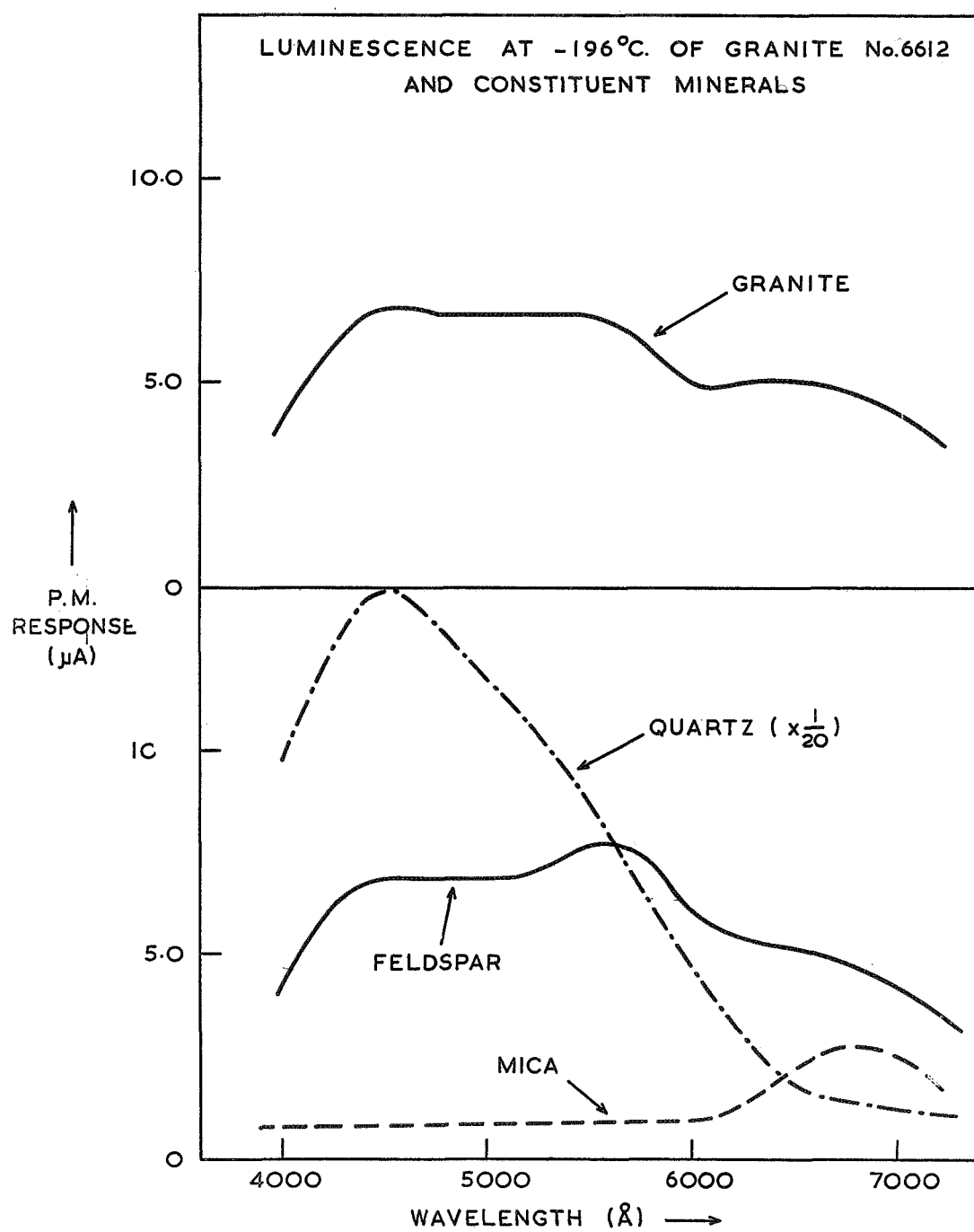


Fig. 2.

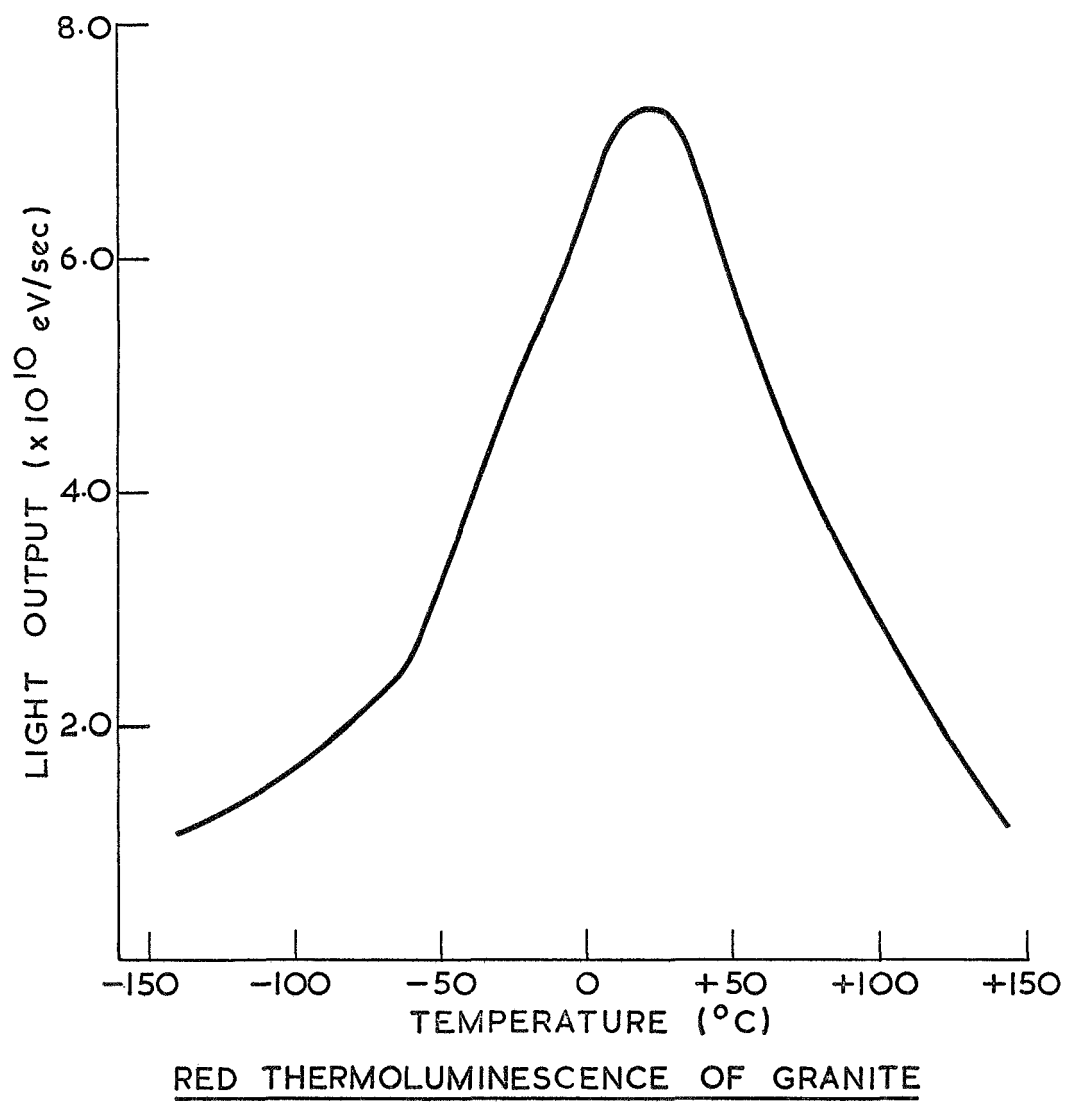


Fig. 3.



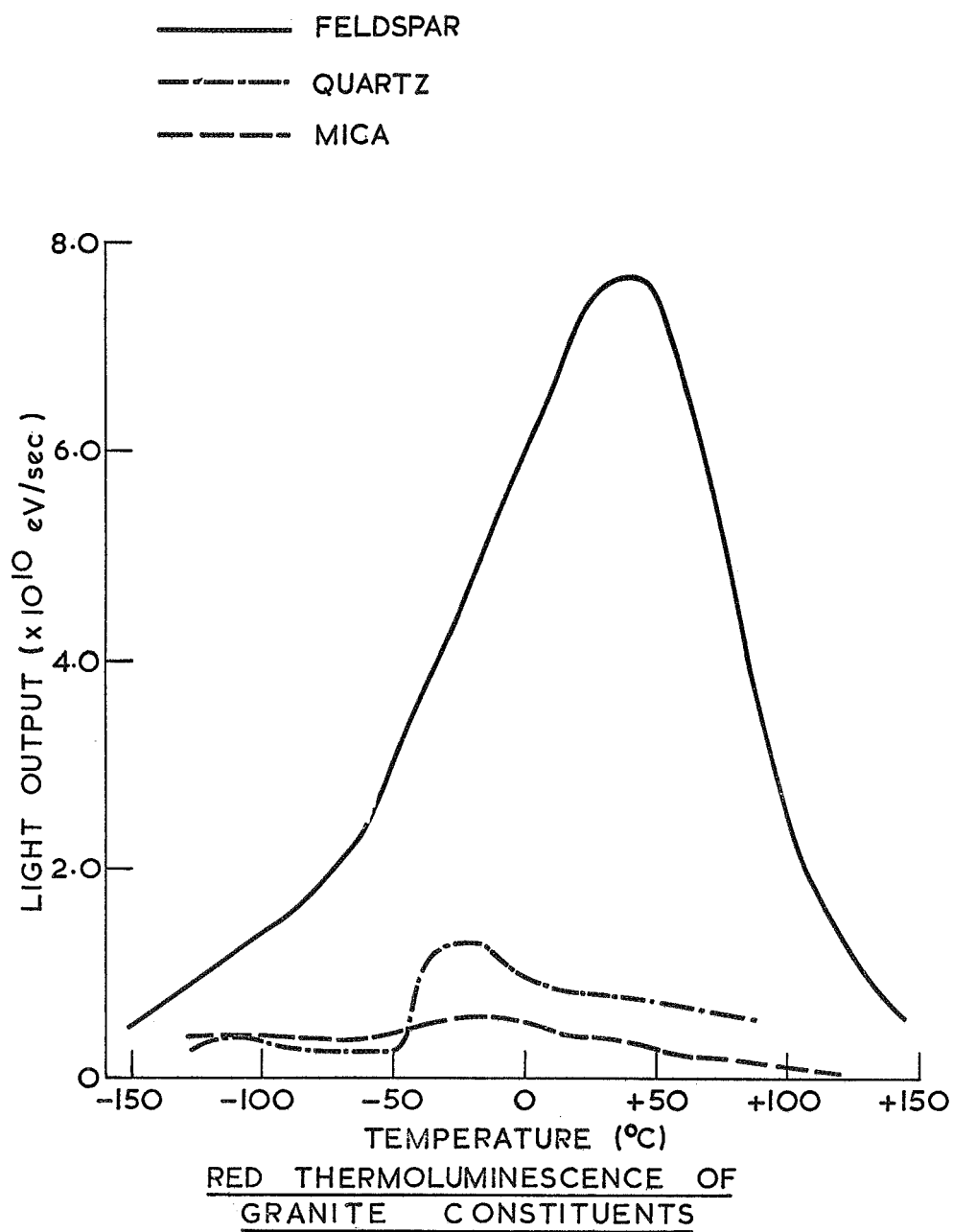


Fig. 4.

The results of our study of lunar feldspar (Edgington and Blair, 1970) returned by the Apollo 11 mission showed the absence of this red glow peak. However, it is now known (Agrell et al., 1970) that the feldspar is a calcium rich plagioclase, i.e. at the opposite end of the albite-anorthite isomorphous series to that of the granitic plagioclase studied in this experiment. But one can reasonably suppose that lunar feldspars from different sites will be different in composition. Indeed, preliminary mineralogical studies (Brown, 1970) of the material returned by Apollo 12 have shown that this is the case. Thus it will be of great interest to study the thermoluminescence of the feldspar returned by this and future missions.

#### Acknowledgments

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## LOW-TEMPERATURE THERMOLUMINESCENCE OF APOLLO 11 MATERIAL

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## INTRODUCTION

There are three reasons for studying the luminescence of lunar rocks. First, the results may be used as indicators of specific crystalline defects or impurities, hence giving information on the structure and mode of origin of the rocks. Second, the existence of a class of transient lunar phenomena has often been ascribed to luminescent effects (Kopal, 1966), and studies of the nature and energy efficiencies of such processes are clearly relevant to this interpretation. Finally, natural thermoluminescence may be searched for, and its presence and intensity may be expected to tell us something of the radiation and thermal history of the material. Each of these aspects has been studied by several workers, and their results have been presented at the Houston conference on Apollo 11 samples (Croaz et al., 1970; Dalrymple and Doell, 1970; Edgington and Blair, 1970; Geake et al., 1970; Greenman and Gross, 1970; Nash, Conel, and Greer, 1970; Sippel and Spencer, 1970).

These include our own report (Edgington and Blair, 1970) of luminescence and thermoluminescence observed at temperatures between 77°K and 500°K; we believe that we are the only workers so far to have carried out such experiments below room temperature. We report here on further experiments designed to elucidate some of the thermoluminescent effects seen at low temperatures. Our conclusion is that these effects, though verified, are artefacts caused by the incorporation of terrestrial water into the samples, and we discuss the possible relevance of this to further studies of lunar luminescence and their interpretation.

## SUMMARY OF PREVIOUS RESULTS

Our apparatus and techniques have been fully described previously (Blair and Edgington, 1968). In earlier experiments (Edgington and Blair, 1970) we studied surface and interior chips from rock 10017, unsorted fines from sample 10084, and specimens of four separated mineral fractions from these fines. We observed intense blue thermoluminescence below room temperature

in all samples except the interior rock chip, the unsorted fines and the opaque (96% ilmenite or ilmenite composites) fraction. This effect was apparently annealed out after heating to 200°C. Our initial interpretation was that the thermoluminescence, like the direct luminescence (Geake *et al.*, 1970; Nash, Conel, and Greer, 1970; Dalrymple and Doell, 1970), was due mainly to the plagioclase component, with differing degrees of shock-damage (Sippel and Spencer, 1970) accounting for the variation between surface and interior rock chips, and with the opaque ilmenite masking the effect from the unsorted fines. Our present experiments were designed to substantiate or refute this interpretation.

### PRESENT EXPERIMENTS AND RESULTS

We took two samples of Apollo 11 fines, 10084.3 and 10084.4, and separated them into various fractions by the conventional techniques of washing in once-distilled water, drying in air at room temperature, sieving through various meshes of nylon sieve, and magnetic separation in a Model L-1 Frantz Isodynamic separator. We then studied the thermoluminescence of three specimens; the least magnetic fraction of the 40  $\mu\text{m}$  - 150  $\mu\text{m}$  size range, of modal composition plagioclase 88%, colourless glass (presumably plagioclase vitrophyres) 10%, pyroxene 2%; and two specimens of the washed and sieved fraction of grain size >150  $\mu\text{m}$ , taken from each of samples 10084.3 and 10084.4. These latter two were selected, since to a visual inspection they were virtually free of opaque ilmenite grains. Each of our specimens weighed approximately 150 mg.

We then proceeded as follows. A specimen was placed in our cryostat which was evacuated to a pressure of about  $3 \times 10^{-2}$  torr and cooled to 77°K. After irradiation with 159 MeV protons, for a dose of about  $10^5$  rads, the sample was heated at 20°C per minute and the several glow peaks that we had previously seen were observed at temperatures  $T_{\text{TL}}$ . Heating was stopped at a temperature  $T_{\text{F}}$  and the cooling, irradiation and heating repeated, finishing at a higher temperature  $T_{\text{F}}$ . This process was repeated for increasing final temperatures  $T_{\text{F}}$ , and for all three specimens.

The results are listed in Table 1. We saw four glow-peaks altogether, but only in the "plagioclase" fraction did all occur together; each coarse-grained specimen showed only three (Fig. 1A and 1B). The temperatures  $T_{\text{TL}}$  were identical, within the listed estimated errors, for each specimen. The magnitudes of the glow-peaks remained constant, within the experimental errors of about  $\pm 15\%$ , for all specimens below  $T_{\text{F}} \sim 300^\circ\text{K}$ , but varied from specimen to specimen, as shown by the (arbitrarily normalized) intensities

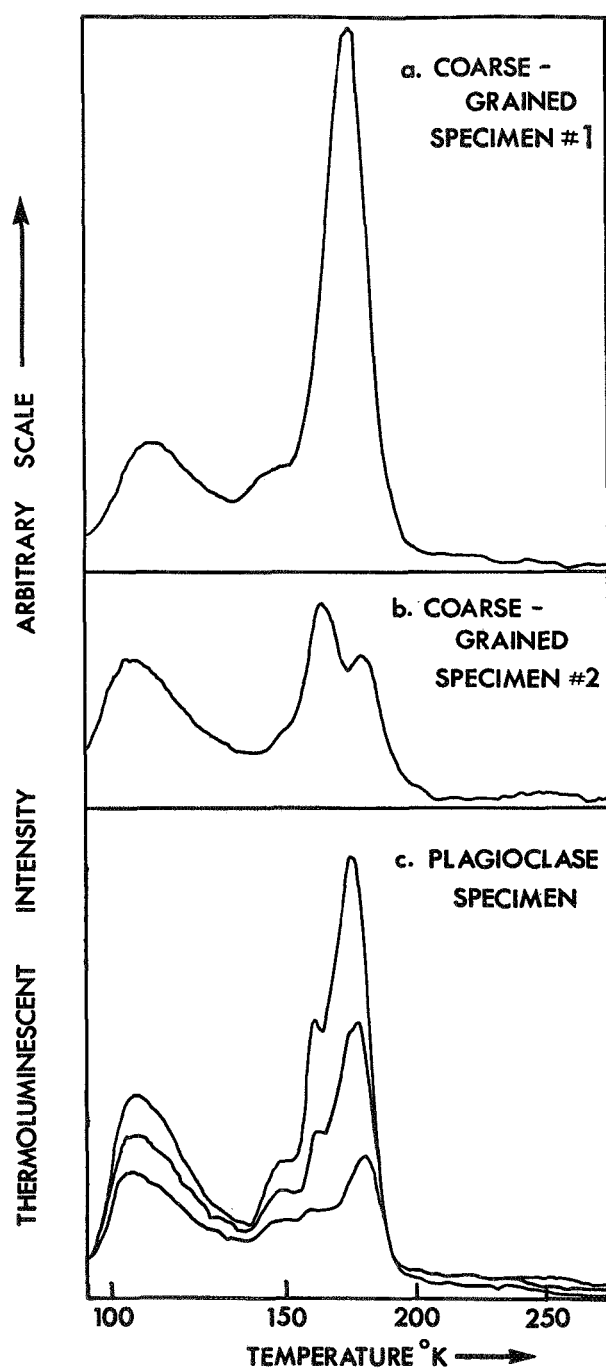


Fig. 1. Thermoluminescence of two coarse-grained specimens of Apollo 11 fines ((a) and (b)) and the "plagioclase" fraction, (c), showing for the latter the effect of repeating the observations after heating to successively higher temperatures above room-temperature.



listed. On raising the specimens to successively higher temperatures  $T_F$  above room temperature we found the glow-peaks to be reduced in magnitude (see Fig. 1C for the "plagioclase" specimen) showing strong indications of disappearing virtually completely by  $T_F \sim 400^\circ\text{K}$ . This effect is shown in Fig. 2 for the glow-peak at  $182^\circ\text{K}$ . The rate of fall-off varied slightly from peak to peak, those occurring at highest temperatures  $T_{TL}$  disappearing first. We illustrate this in Fig. 3 where  $T_{TL}$  has been plotted against  $(T_F)_{1/2}$ , the temperature by which the corresponding glow-peak magnitude has fallen to half its initial value.

Table 1

GLOW-PEAKS AND THEIR PARAMETERS

Temperature in $^\circ\text{K}$		Intensity of Glow-Peak in Each Specimen (Arbitrarily Normalised)		
of glow-peak ( $T_{TL}$ )	of annealing ( $T_F$ ) <sub>1/2</sub>	"Plagioclase"	Coarse- Grained #1	Coarse- Grained #2
$108 \pm 1$	$369 \pm 5$	1.00	0.82	1.00
$142 \pm 2$	$352 \pm 5$	0.62	0.67	--
$156 \pm 2$	$349 \pm 10$	1.22	--	1.62
$182 \pm 3$	$331 \pm 5$	2.13	3.61	1.07

DISCUSSION

We interpret these observations as evidence that terrestrial water has been adsorbed onto the surfaces of certain mineral phases, forming hydrated states which act as powerful electron traps and are responsible for the glow-peaks. The justification for this interpretation is:

- i) The absence of the glow-peaks from the unsorted fines, and their presence only in the washed fractions (both magnetically separated and unseparated).
- ii) The gradual disappearance of the glow-peaks on raising the temperature to  $>100^\circ\text{C}$ . This is the conventional procedure used in mineralogy to drive off physically adsorbed water in rock samples. The fact that the lunar surface temperature itself rises to over  $100^\circ\text{C}$  near

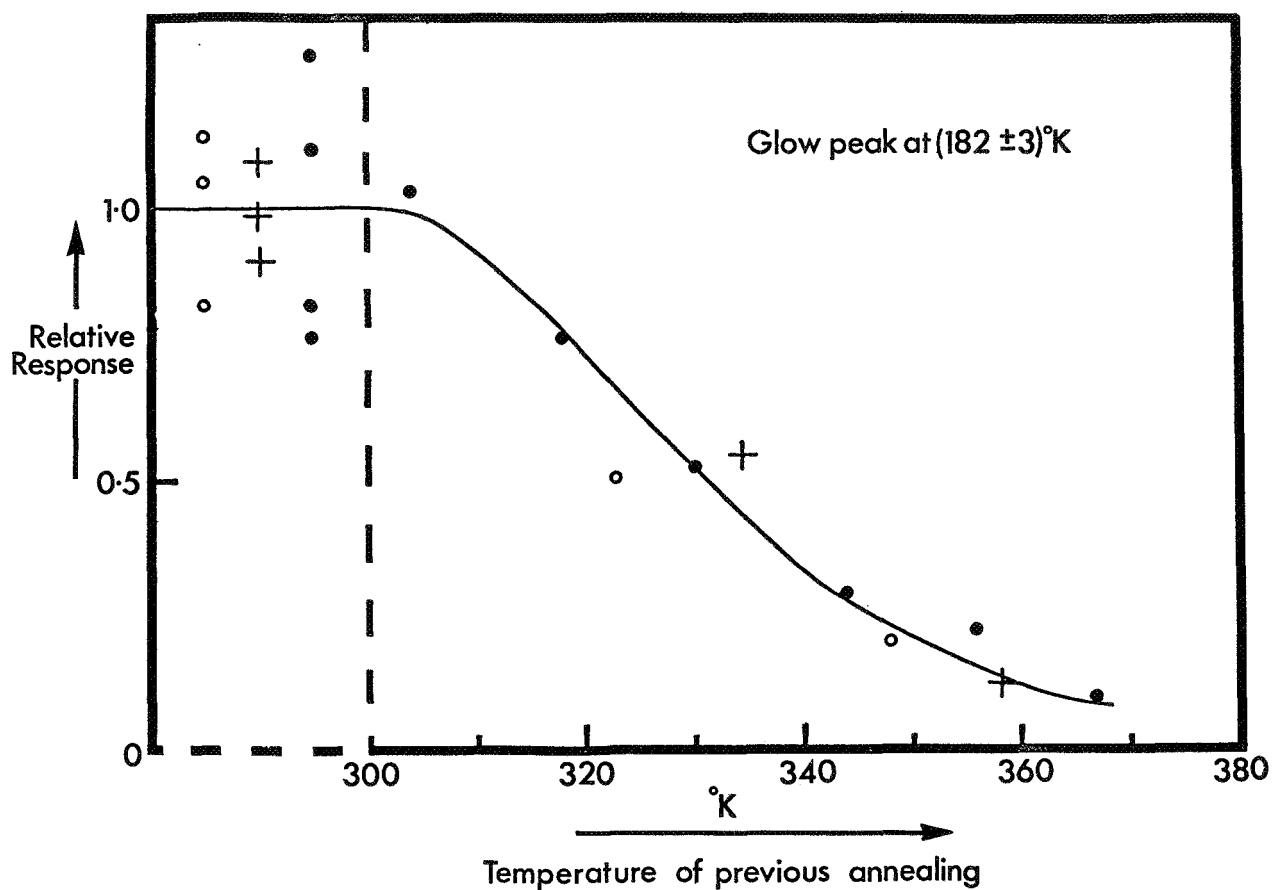


Fig. 2. Decrease in intensity of the glow-peak at  $182^{\circ}\text{K}$ , as a function of the previous temperature to which the specimen had been heated. All three specimens have been assigned an arbitrary response (averaged over several readings) of unity, below room temperature. 0 - "plagioclase" fraction; + and - the two coarse-grained specimens.

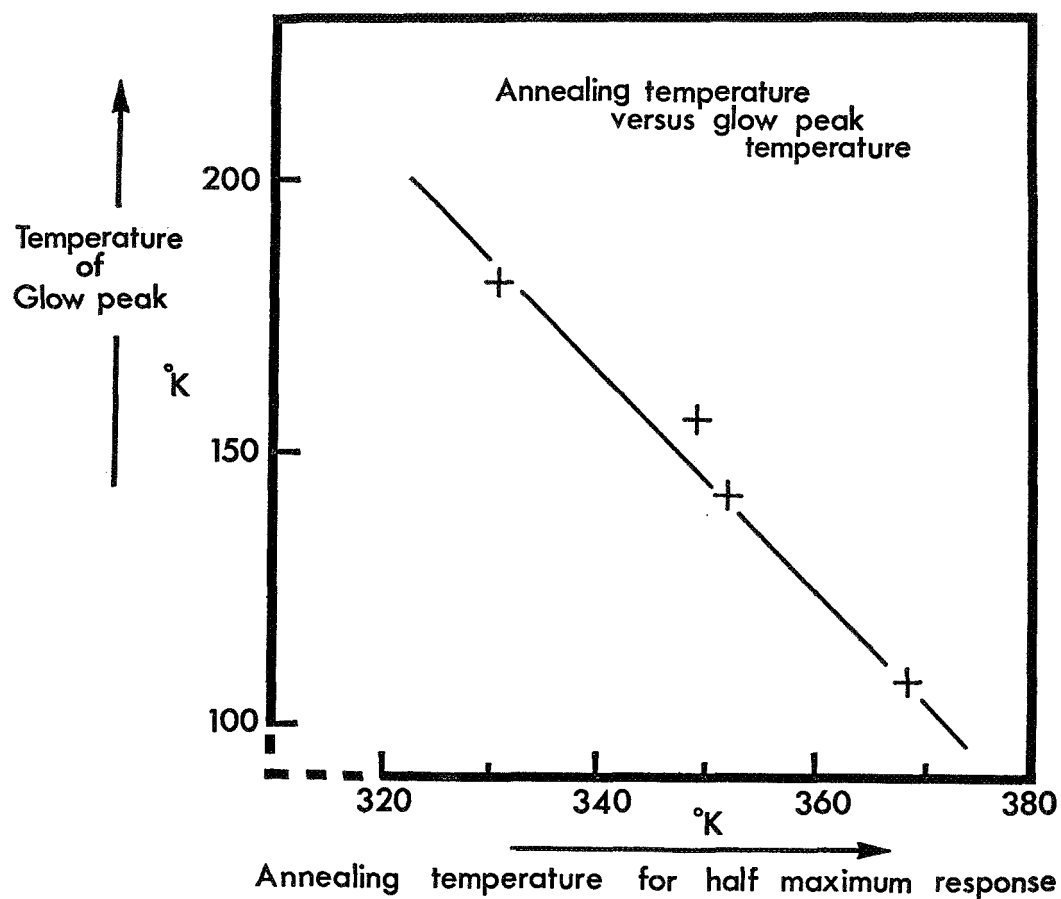


Fig. 3. Relation between glow-peak temperature and rate of fall-off of response. The line has no significance other than to indicate the trend.

lunar midday suggests that we cannot be observing a conventional annealing process.

- iii) The reappearance of the effect, in one particular instance, when the cryostat was allowed to warm up after a layer of ice had formed on it during the previous sample change. In this case the only modifying factor that could be inferred was the presence of considerable water vapour near the sample.

The absence of thermoluminescence in an interior rock fragment indicates that the effect is associated with features, such as meteoritic shock damage and the presence of glassy material, that are common both to rock surfaces and to soil fragments. Moreover both absolute and relative glow-peak intensities vary from specimen to specimen in a manner that suggests that only a minor constituent (for instance the highly shocked glass vitrophyres) is responsible.

On earth anhydrous minerals, particularly silicate glasses (Simon, 1960) are unknown, water being ubiquitous. The chemical analyses (Friedman *et al.*, 1970) of Apollo 11 fines and breccia reveal little or no adsorbed water; and there is generally less than 500 ppm of chemically-bound water. Some proton magnetic resonance studies (Manatt *et al.*, 1970) suggest the water content is less than 1 ppm. From terrestrial analogues it is reasonable to infer (Poole, 1970) that this anhydrous material will take up  $\sim 1\%$  of water on exposure to a damp atmosphere, particularly since meteoritic shock-damage has led to considerable micro-fracturing of the surfaces.

The major effect of such adsorption is known to be (Burns, 1970) the break-up of silicates into hydrated complexes plus hydro-silicate residues, as illustrated in Fig. 4. Such processes might give rise to electron traps at the OH sites, their de-excitation spectra being determined by the extent of hydration and the resulting crystal-field energy levels of the cation acting as the luminescence centre. We should make it clear that this mechanism of silicate hydration has been proposed (Burns, 1970) to account for leaching of terrestrial minerals and the subsequent complete removal of the residues and hydrated complexes from the crystal site; what we suggest here is that the lattice remains intact, though perturbed by the presence of the hydroxyl groups.

It therefore seems possible that the different glow-peaks are due to various hydration states of the silicates. This would explain the observed association between trap depth and annealing temperature (Fig. 3) in the following way. The more hydrated the cation, the greater the crystal field

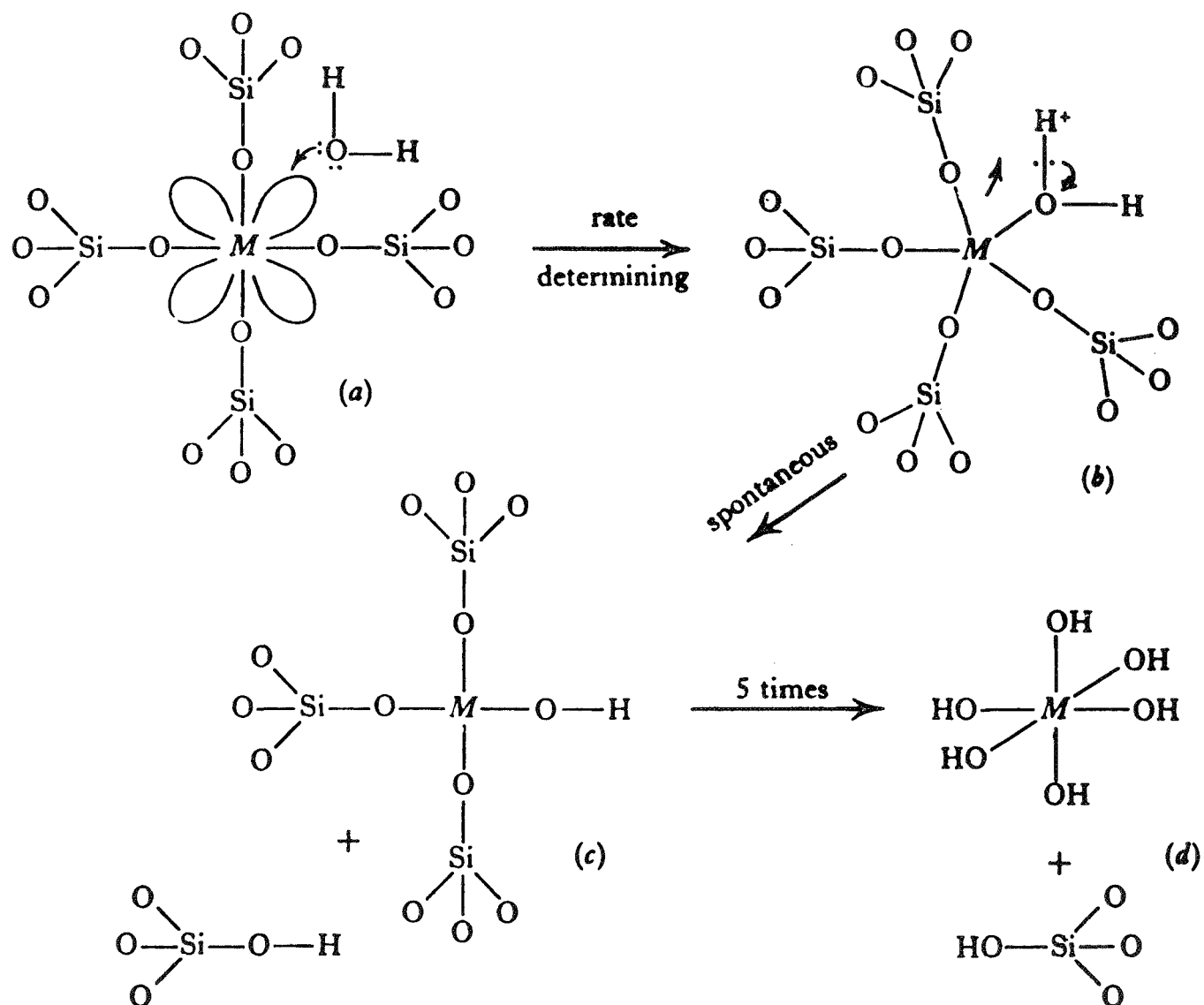


Fig. 4. Mechanism for the hydrolysis of a ferro-magnesian silicate.  
(From Burns, 1970).

perturbation and the deeper the trap, consequently one would expect the water in such states of high hydration to be less tightly bound and to disappear first, on heating above room temperature.

We conclude that in further studies of low-temperature luminescence of lunar samples, stringent precautions will have to be taken to keep this exotic anhydrous material dry, or at least in its received state. We note that experiments such as ours appear to be very sensitive indicators of the possible presence of native water on the moon, as suggested by the "permafrost" notion which has been widely discussed. Most investigators of thermoluminescence (Geake et al., 1970; Dalrymple and Doell, 1970; Crozaz et al., 1970) have heated their virgin samples prior to irradiation, in order to determine the magnitude of any natural thermoluminescence; this procedure will of course destroy the evidence for any native adsorbed water, and should be used with caution.

The intensities of these water-induced glow-peaks are rather large; in an earlier paper (Edgington and Blair, 1970) we quoted values for the energy-efficiency of  $\sim 10^{-6}$ , but it appears that this can be changed by several orders of magnitude, depending on how much water is present. Such large intensities make it interesting to speculate on this mechanism being a possible cause of some of the transient lunar phenomena referred to earlier. We plan further experiments, including study of Apollo 12 material, to test these ideas.

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## LUNAR SAMPLE LUMINESCENCE

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## ABSTRACT

The luminescence of lunar rocks is being studied to 1) evaluate the reported lunar luminescence, 2) understand how the luminescence behavior reflects the origin and history of lunar rocks, and 3) discover luminescence features that might aid in geologic mapping and exploration. Excitation is with ultraviolet (1216 A and 2000 to 4000 A), x-rays, protons, and electrons. Results to date of measurements still in progress show efficiencies with 3000 A excitation between  $5 \times 10^{-6}$  and  $2 \times 10^{-5}$  for four lunar rocks (one breccia, one coarse-grained igneous, and two fine-grained igneous). This compares with values of about  $2 \times 10^{-5}$  measured for a terrestrial gabbro, a type similar in composition to the lunar rocks, and about  $6 \times 10^{-5}$  for a terrestrial granite. If these are typical values for other ultraviolet excitation wavelengths, the Apollo 11 site appears to contribute little to lunar luminescence; however, higher efficiencies in other areas of the moon, possibly the highlands, are suggested by the Surveyor measurements and by the Apollo 12 samples.

\* \* \*

We are studying the luminescence of lunar rocks to evaluate the reports of lunar luminescence based on astronomical observations, to understand how the luminescence behavior reflects the origin and history of the lunar lithologic materials, and to discover luminescence features of the rocks that might aid in geologic mapping and other lunar exploration activities. To achieve these objectives, we are measuring the luminescence spectra and efficiencies and comparing the results with similar measurements of terrestrial rocks and minerals. The excitation sources are those of importance in the space environment: ultraviolet (1216 and 2000 to 4000 A), x-rays (0.4 to 8 A), protons (2 to 150 KeV), and electrons (2 to 150 KeV). The luminescence spectra are measured from 1216 A, or from the exciting wavelength if it is longer than 1216 A, to 6000 A.

We give here some results of our measurements with excitation by 3000 Å ultraviolet. Figure 1 shows the experimental arrangement. The source was a 2500 watt high pressure xenon-mercury lamp, the light from which passed through a quartz prism monochromator with a Corning 7-54 filter at the exit slit to cut out wavelengths longer than 4000 Å. The light from the sample passed through a 0.25 meter grating spectrometer to an EMI 9558Q photomultiplier tube and was measured and recorded by a picoammeter and X-Y recorder. For some runs, a Corning 3-74 filter was placed between the sample and the entrance slit of the grating spectrometer to eliminate second orders and scattered wavelengths shorter than 4000 Å. Because of this cutoff, the luminescence could not be investigated below 4000 Å in runs with this filter. In runs without it, the luminescence band investigated was from about 3500 to about 5500 Å, being limited at the long wavelength end by the second order of the exciting beam (see, for instance, Figures 2 and 3). The exciting beam was a band of about 200 Å full width at half maximum centered at about 3000 Å.

Six samples from four lunar rocks were studied: 10044,38 (exterior) and 10044,53 (interior) from a coarse-grained igneous rock, 10048,36 (interior) and 10048,37 (exterior) from a breccia, and 10057,45 (interior) and 10022,55 (exterior) from two fine-grained igneous rocks. The exposed surface area ranged from a little less than one to a little less than two square centimeters. Terrestrial comparison samples consisted of granite (El Capitan formation, Mariposa County, California), gabbro (near San Marcos, San Diego County, California), and willemite (Franklin Furnace, New Jersey), the latter a highly luminescent mineral.

All samples except willemite were found to have very low luminescence efficiencies with 3000 Å excitation. Willemite, with an efficiency of about  $2 \times 10^{-2}$ , gave the spectrum shown in Figure 2 in which the peak at about 5200 Å is clearly seen above a low background, separated from the second order peak of the 3000 Å exciting line. The spectra of the other eight samples were much less distinct and had to be recorded with greatly increased detector sensitivity. This served to amplify scattered light and to magnify other instrumental effects so that the signal was much more background-limited. Therefore, the luminescence signal was extracted by comparing the sample spectrum with that of a barium sulfate standard.

The barium sulfate has a reflectance of almost 100 percent over the wavelength band recorded (2000 to 6000 Å) and, as far as is known, has no

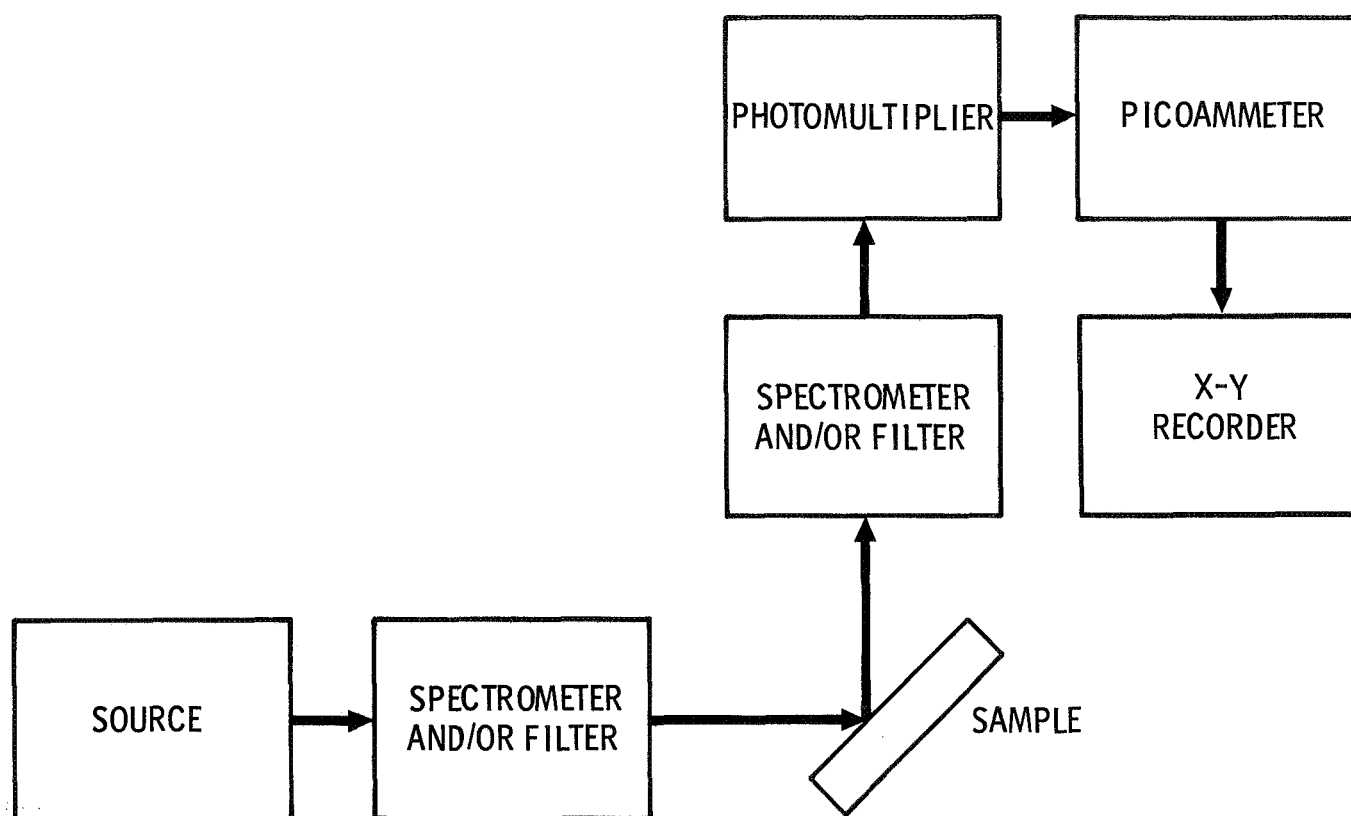


Fig. 1. Experimental arrangement for measuring ultraviolet-excited luminescence.

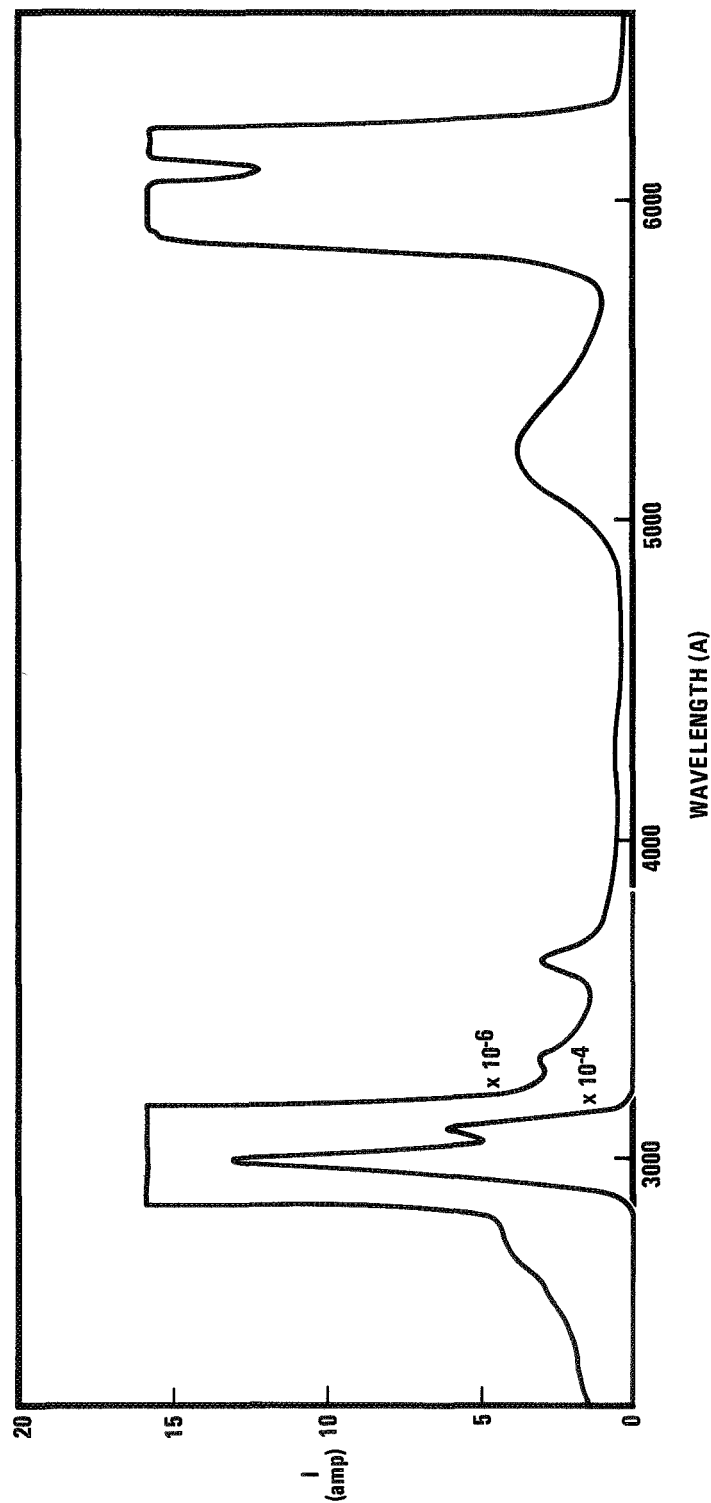


Fig. 2. Luminescence of willemite. Luminescent band with peak at about 5200 A stands out clearly. Peaks at 3000 and 6000 A are the first and second order, respectively, of the exciting line. Small peaks at about 3300 and 3600 A are stray light background from the monochromator; they originate from strong lines in the source.

significant luminescence in this band. Its spectrum, therefore, is that of the light striking the sample. First, it was assumed that the ratio of the sample and barium sulfate spectral curves would be constant and equal to the reflectance if no luminescence were present. This is justified by the general similarity of sample and standard curves (Figures 3 and 4) and by the almost constant reflectance values of the lunar material (Adams and Jones, 1970; Geake, *et al.*, 1970; Nash, *et al.*, 1970) and of the granite and gabbro (our unpublished data) over the wavelength band investigated. The sample-to-standard spectral curve ratios were then calculated, and the minimum value for each sample, consistent with the published reflectance values, was assumed to represent zero luminescence. Finally, the wavelengths at which the ratio exceeded the minimum were considered to be those at which luminescence could have occurred, and the currents corresponding to these excess values were calculated and plotted as the corrected curves shown in Figures 3 and 4.

The willemite, granite, and gabbro terrestrial comparison samples and lunar sample 10044,53 were run with and without the Corning 3-74 filter. In addition to cutting out the wavelengths less than 4000 Å, the filter had the effect of reducing the signal in the visible wavelengths about two decades (Figures 3 and 4). This reduction would not have been possible if the signal arose mostly or entirely from visible light because the filter transmission in these visible wavelengths is about 88 percent. Therefore, the background in the spectral curves without the filter must be almost entirely light of wavelengths less than 4000 Å scattered within the system. The luminescence efficiencies were, as a result, calculated from the curves taken with the filter. In the case of the five lunar samples for which such curves were not taken, the apparent efficiency values from the curves without filter were reduced by a factor of 20, the ratio of without-filter to with-filter efficiencies for 10044,53 and gabbro. This seems justified on the basis of the general similarity in both intensity and spectral character of all the lunar samples and of the lunar samples and the gabbro. The efficiencies of all the samples over the 4000 to 6000 Å band are shown in Table 1. These are total luminescence efficiencies; that is, the ratio of energy in the luminescent band to energy in the 3000 Å line about 200 Å wide incident upon the sample. As residual background effects could still be present in the data, the tabulated luminescence efficiencies are to be considered as upper limits.

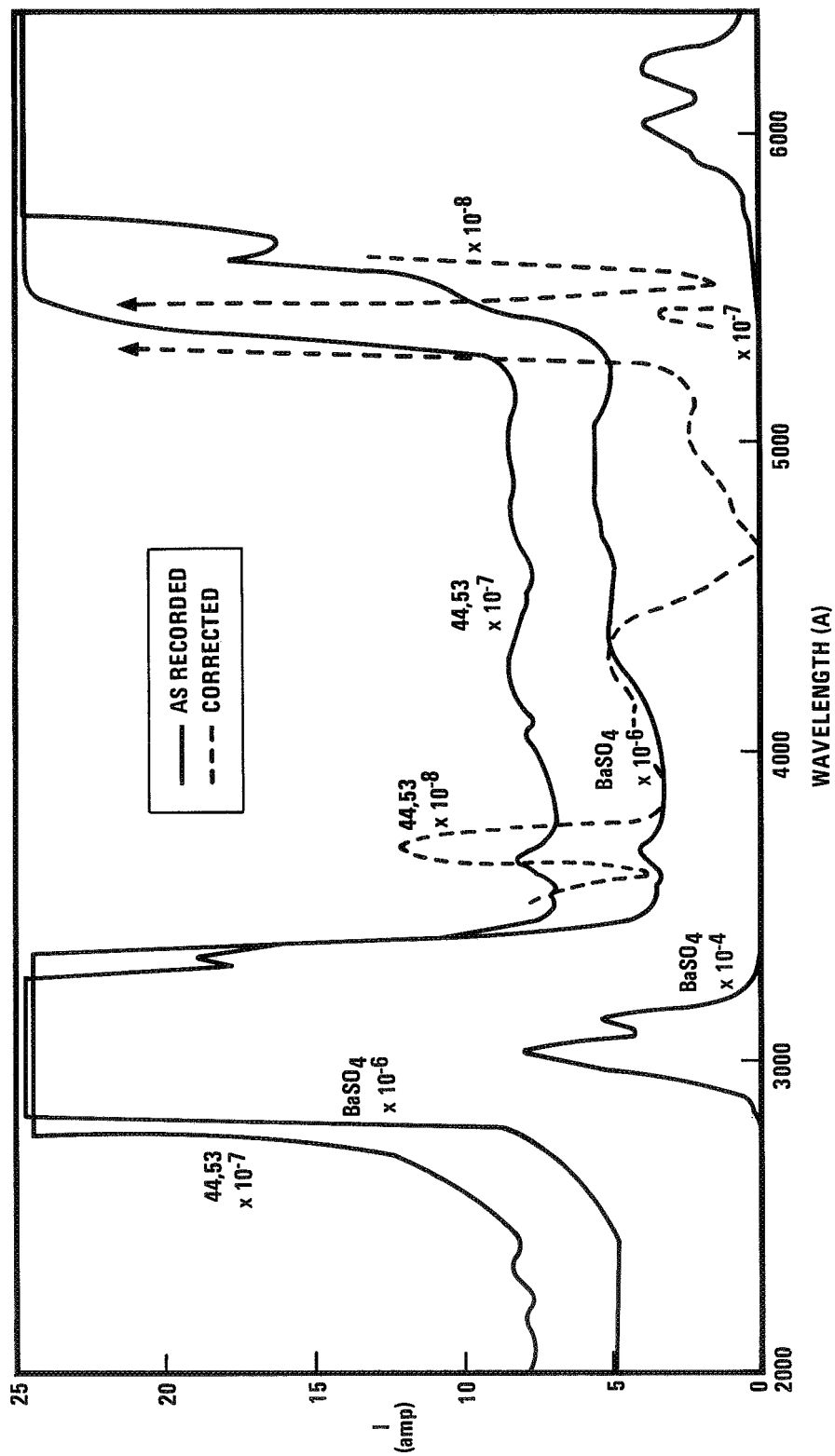


Fig. 3. Spectrum of lunar sample 10044,53 compared with barium sulfate standard; without Corning 3-74 filter to absorb wavelengths less than 4000 Å. Peaks at 3000 and 6000 Å are the first and second order, respectively, of the exciting line.

TABLE 1

Luminescence efficiencies of lunar and terrestrial rocks and minerals in the 4000 to 6000 Å band with 3000 Å excitation.

SAMPLE	EFFICIENCY UPPER LIMIT	ROCK TYPE	POSITION IN ROCK
LUNAR			
10044,38	$10^{-5}$	COARSE-GRAINED IGNEOUS	EXTERIOR
10044,53	$10^{-5}$	COARSE-GRAINED IGNEOUS	INTERIOR
10022,55	$10^{-5}$	FINE-GRAINED IGNEOUS	EXTERIOR
10057,45	$2 \times 10^{-5}$	FINE-GRAINED IGNEOUS	INTERIOR
10048,36	$5 \times 10^{-6}$	BRECCIA	INTERIOR
10048,37	$5 \times 10^{-6}$	BRECCIA	EXTERIOR
TERRESTRIAL			
GRANITE	$6 \times 10^{-5}$		
GABBRO	$2 \times 10^{-5}$		
WILLEMITE	$2 \times 10^{-2}$		

The most noteworthy feature of Table 1 is the low luminescence efficiency of the lunar material. These results agree with those of Geake, et al. (1970), and Nash, et al. (1970), who found no luminescence in the lunar rocks with middle and near ultraviolet excitation. The tabulated efficiencies are comparable to or less than the ones for terrestrial rocks that we and Nash measured with protons and that we measured with electrons and x-rays; they are also much lower than those we estimated for terrestrial rocks with the 1800 to 2000 Å excitation band by a less refined filter method (Greenman, et al., 1965; Nash, 1966).

Grainger (1963), who made the most accurate line-depth measurements of the moon, observed an average luminescence intensity around 3950 Å of about five percent of the reflected background. This implies an efficiency of about one percent. The efficiencies we measured in this study of the Apollo 11 lunar samples are some three orders of magnitude lower and indicate a level of lunar luminescence that would be undetectable by the line-depth



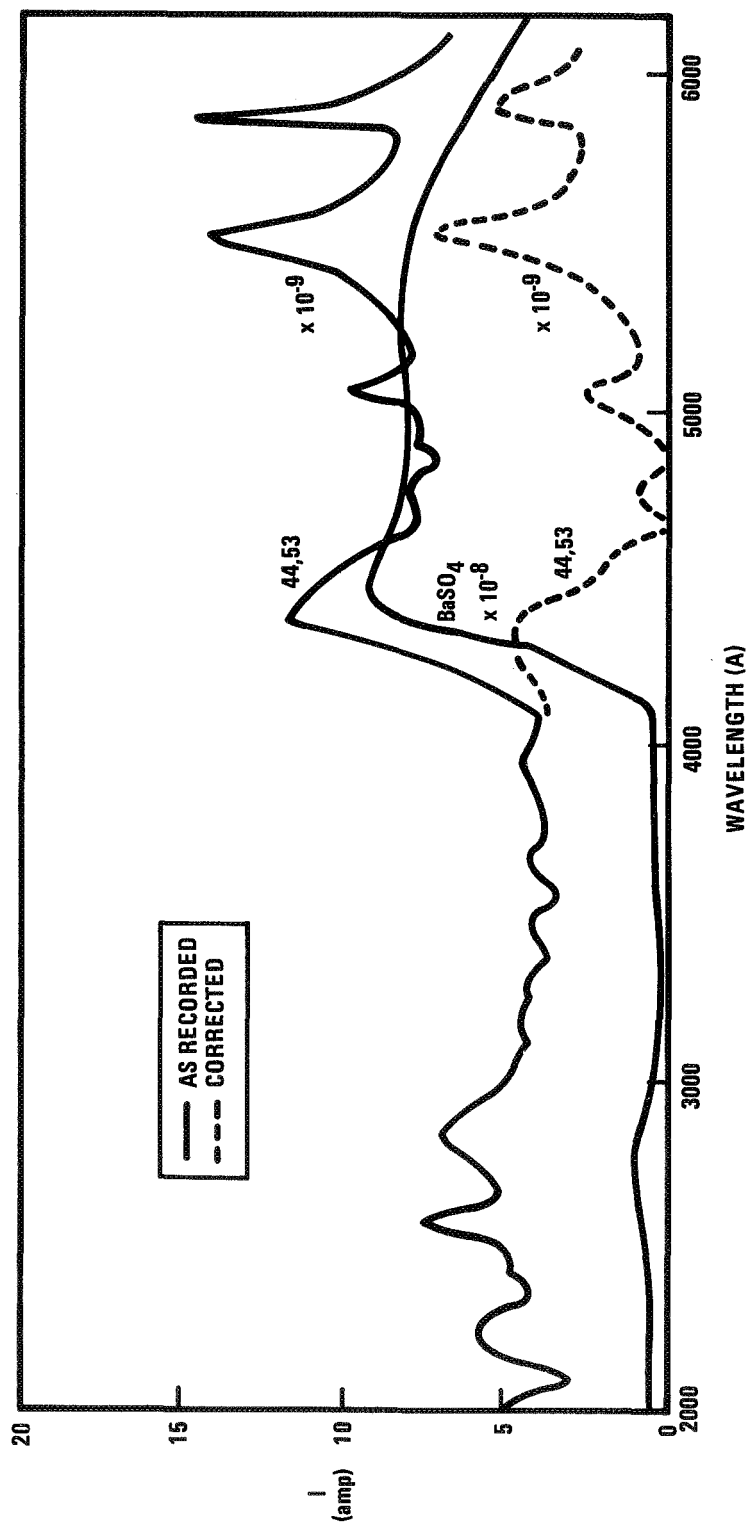


Fig. 4. Spectrum of lunar sample 10044,53 compared with barium sulfate standard; with Corning 3-74 filter to absorb wavelengths less than 4000 A.

technique. If our further studies with excitation at other ultraviolet wavelengths and with proton, electron, and x-ray excitation show no greater efficiencies than these, the Apollo 11 landing area can be considered to contribute nothing to the luminescence reported from the observations. Grainger's observations did not include the Apollo 11 landing area; if correct, they imply higher luminescence efficiencies in other areas of the moon.

Terrestrial gabbros, which are similar in composition to the Apollo 11 rocks, are found to possess low luminescence efficiency as compared to granites; this is evident also from the data in Table 1. Thus, other lunar areas, especially in the highlands, could contain rocks of higher efficiency than those from Apollo 11. For example, the Surveyor 7 alpha-scattering analysis measured less than half as much iron, a luminescence-quenching element, at the Tycho site than was measured at the Surveyor 5 and 6 mare sites (Turkevich, *et al.*, 1969). Also, one rock in the Apollo 12 collection contains K-feldspar and higher than ordinary amounts of K, Th, and U (LSPET, 1970), mineralogic and chemical characteristics of the more luminescent of the common terrestrial igneous rocks. Therefore, samples from many areas of the moon need to be studied in order to characterize the luminescence of the lunar rocks and to understand its significance.

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THERMOLUMINESCENCE-CHEMICAL COMPOSITION CORRELATIONS  
FOR METEORITIC ENSTATITE

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ABSTRACT

Relationships between total thermoluminescence output and elemental composition for a single phase, enstatite ( $\text{MgSiO}_3$ ), were sought for enstatite chondrite and achondrite meteorite specimens. The total thermoluminescence output of meteoritic enstatite was found to be inversely proportional to the amount of iron in the material and independent of the Ca and Mn. No significant correlation for thermoluminescence intensity was found with respect to cosmic ray exposure ages or natural radioactivity. This compositional dependence for thermoluminescence response indicates severe limitations on using thermoluminescence as a stratigraphic analytical technique for lunar silicate materials.

\* \* \*

Numerous papers have appeared concerning the possible utility of thermoluminescence (see McDougall, 1968); many attempt to describe relations without benefit of detailed physical and chemical measurements. This investigation presents thermoluminescence response data and chemical information for a series of highly characterized single phase specimens separated from a polymineralic assemblage. As will be demonstrated, multivariate statistical analytical techniques are required to assist in identifying and evaluating major relationships for this relatively uncomplicated natural material.

Enstatite grains (approximately 150-180  $\mu\text{m}$ ) were separated from 14 different chondritic and achondritic meteorite specimens, and interrelations between total thermoluminescence output and elemental composition for the single phase were investigated. There was sufficient variability in element concentrations exhibited by the specimens to permit an evaluation of the

influence of composition on thermoluminescence emission (Greer and Weber, 1969). Seven of the eleven enstatite chondrites (Adhi Kot, Abee, Atlanta, Hvittis, Khairpur, Jajh deh Kot Lalu, and Blithfield) and seven of the nine enstatite achondrites (Bishopville, Cumberland Falls, Khor Temiki, Indarch, Norton County, Pesyanoe, and Shallowater) which have been identified as meteorites are included in this work.

The major investigation was restricted to the pyroxene, enstatite. All pyroxene structures link  $\text{SiO}_4$  tetrahedra by sharing two of the four corners forming continuous  $(\text{SiO}_3)_n$  chains. The  $5.3 - \text{\AA}$  repeat distance along the length of the chain defines the c parameter of the unit cell. The cations (Ca, Fe, Mg, etc.) link the chains laterally. In enstatite ( $\text{MgSiO}_3$ ), Mg or (Mg, Fe) atoms laterally link the  $(\text{SiO}_3)$  chains. Ions other than Mg and Fe can be present in orthopyroxenes and commonly include Ca and Mn; usually the sum of these constituents is less than 10 mol %. The polymorphs with the structure of enstatite contain less than 30 mol %  $\text{FeSiO}_3$  and less than 15 mol % of  $\text{CaSiO}_3$ , as defined by the structural grouping for pyroxenes in the field  $\text{CaMgSi}_2\text{O}_6 - \text{CaFeSi}_2\text{O}_6 - \text{MgSiO}_3 - \text{FeSiO}_3$ . The majority of pyroxenes can be considered to be members of this four-component system (Deer, Howie, and Zussman, 1965). In both the enstatite chondrite and achondrite specimens, many of the metals which commonly substitute for the Mg cation in the pyroxene structure are present in low concentrations, or below detection limits. Therefore, the disposition and concentrations of the Fe, Mn, and Ca cations are of primary interest.

The enstatite subspecimens were examined by an optical microscope, X-ray diffraction, an electron microprobe, and a thermoluminescence detection unit. A Perkin-Elmer differential scanning calorimeter standard 1/4-in.-diameter sample holder and unit with a constant rate heating element was adapted for thermoluminescence measurements. An RCA 6199 photomultiplier tube for detecting the natural thermoluminescence emission, a heating rate of  $80^\circ\text{C}/\text{min}$ , a heating range of  $25\text{--}500^\circ\text{C}$ , and a dry  $\text{N}_2$  gas flow of  $20 \text{ cm}^3/\text{min}$  were chosen for the experiments. All heating was performed in (an oxygen free) nitrogen atmosphere to suppress any chemiluminescence; a quartz window served to protect the photomultiplier from the heated gas within the chamber.

Figure 1 illustrates the typical glow curves obtained from the representative enstatite specimens. As a first approximation, a glow can be assumed to be proportional to the amount of radiation energy deposited in the material, and if the time rate of deposition of energy is known,

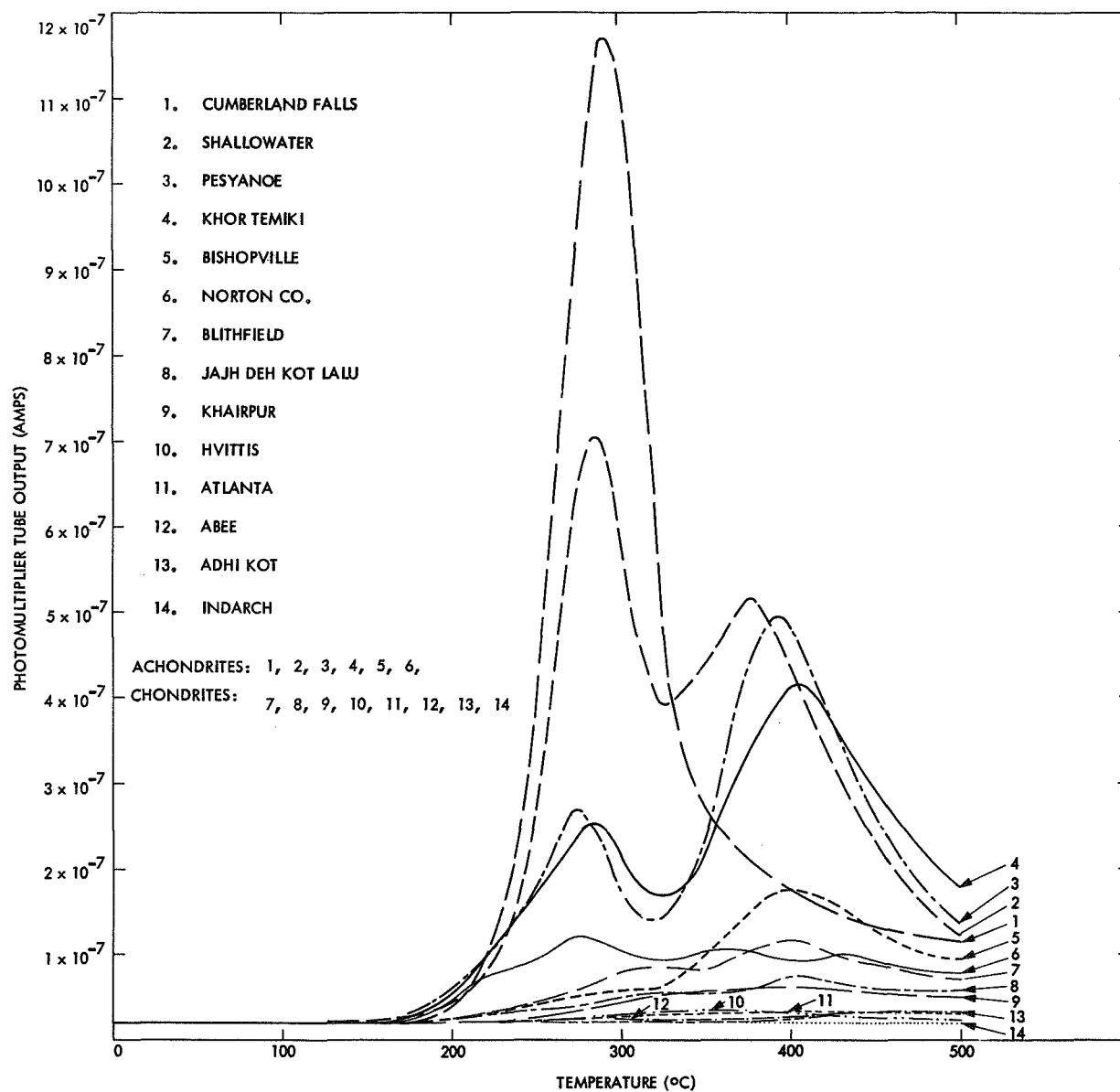


Fig. 1. Glow curves for meteoritic enstatite.

this may provide an indication of the total period of time over which the sample has been receiving the radiation dose. No peaks are detected for these samples below 200°C, although laboratory irradiations typically introduce peaks below this temperature. The results indicate the presence of a mechanism involving a quick drainage of low-temperature peaks (i.e., shallow traps) followed by a more gradual draining of the high-temperature peaks (or deeper traps). Above 200°C two major peaks usually appear for the meteoritic enstatite, one at approximately 290°C and one at approximately 380°C. Both peaks are stable for long periods, especially when iron impurity concentrations in the enstatite host are very low (< 100 ppm).

Figure 2 represents the variation of integrated thermoluminescence emittance for enstatite from individual meteorite specimens with respect to Fe concentration. A number of significant relationships are featured on this diagram. The trend of positions of the specimens on the diagram, considered from the lower-right corner to the upper-left corner, is in agreement with the following relationships: change of meteorite class, decreasing Fe in the pyroxene structure, and increase in thermoluminescence output. A least-squares fit analysis shows the total thermoluminescence output as being inversely proportional to the Fe concentration. A subtle additional trend is indicated: the clinoenstatite chondrite specimens have the shortest cosmic ray exposure ages in the series (approximately  $10^6$  years (Mason, 1966)), the rhombic enstatite chondrite specimens have longer cosmic ray exposure ages (approximately  $2 \times 10^7$  years (Mason, 1966)) in the series, and the rhombic enstatite achondrites have the longest cosmic ray exposure ages (approximately  $4 \times 10^7$  years, a representative value for all of the enstatite achondrites (Urey, 1967)) in the series.

Multivariate statistical analytical techniques were utilized to process the data so as to evaluate the significance of the relationships that are indicated by the measurements. A significant negative correlation at the 0.1 % confidence level is evident for the total thermoluminescence output-Mn, total thermoluminescence output-Ca, or total thermoluminescence output-age (cosmic ray exposure or natural radioactivity (Anders, 1962; Kirsten et al., 1963; Hintenberger et al., 1964; Eberhardt et al., 1965)) were found. The partial sample correlation coefficient  $r_{\text{thermoluminescence, Fe/age}}$



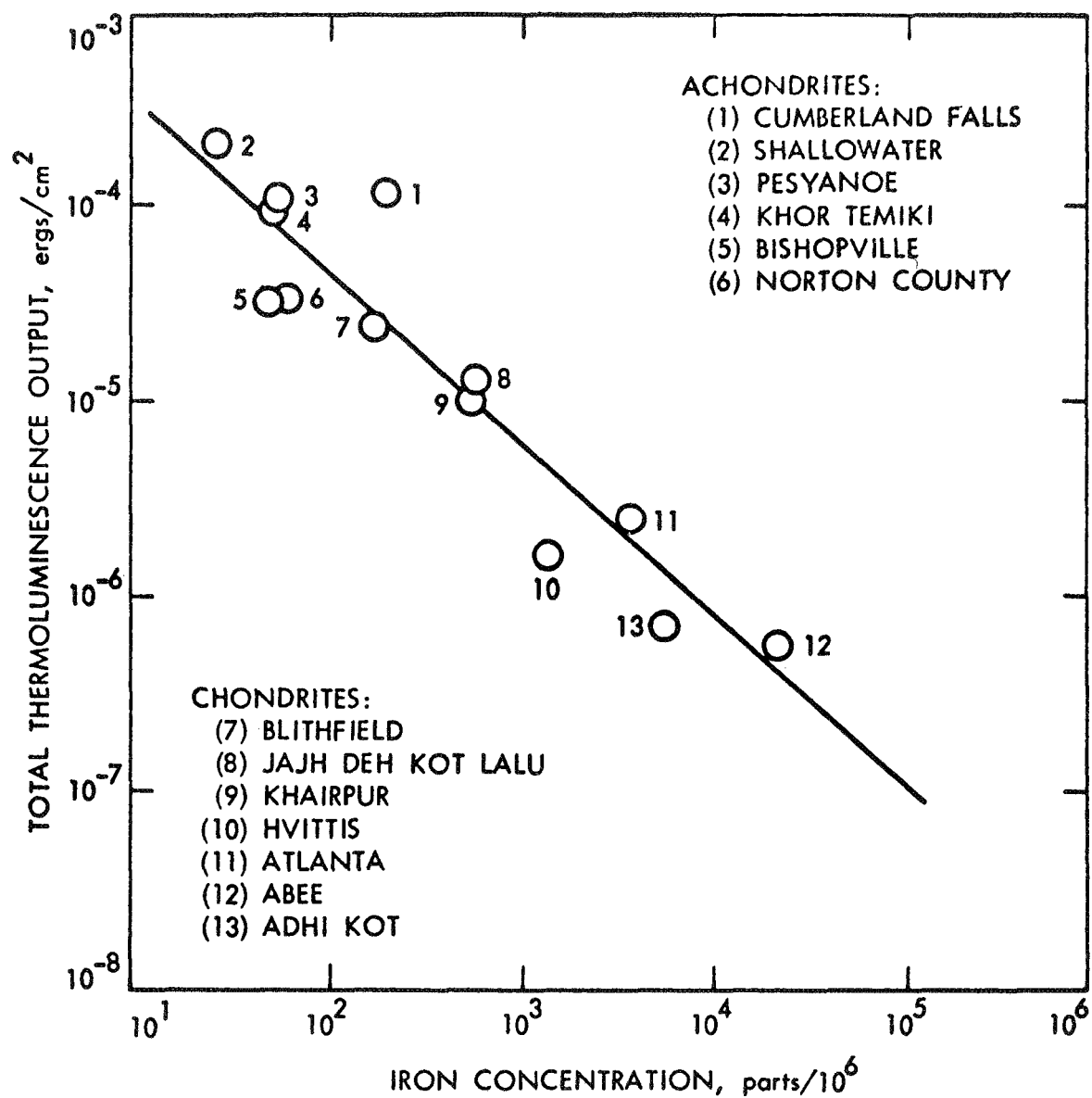


Fig. 2. Thermoluminescence response as related to Fe concentration for enstatite.

which expresses the correlation of total thermoluminescence output and Fe independent of (rather than ignoring) the effect of age, is both negative and significant at 0.1 %, confirming an observed and presumed causal relationship between these variables.

The enstatite specimens represent a relatively simple system; however, for comparative purposes a more complex example, serpentine ( $\text{Mg}_3[\text{Si}_2\text{O}_5](\text{OH})_4$ ), has been investigated as well. Several significant correlations were found on a basis of data for multiple analyses for 32 different samples. Since Cr can substitute for either Fe or Ni in serpentine, it was reasonable to find a significant positive Fe-Cr and a positive Ni-Cr correlation; however, since the total thermoluminescence output was found to be negatively correlated with Fe, Cr, and Ni, respectively, it was necessary to compute partial correlation coefficients as well so as to test for the presence of a total thermoluminescence output-Cr correlation or for an induced correlation as developed through the associated Fe-Cr and Ni-Cr positive correlations. On the basis of the calculated partial correlation coefficient,  $r_{E, \text{Cr}/\text{Fe}, \text{Ni}}$ , no significant correlation was determined to exist for the total thermoluminescence output (E) and Cr at the 10 % confidence level when considered independent of Fe and Ni. But both the  $r_{E, \text{Fe}/\text{Cr}, \text{Ni}}$  and  $r_{E, \text{Ni}/\text{Fe}, \text{Cr}}$  computed values established the presence of a significant negative correlation for both E-Fe and E-Ni. The complexity of this example shows the necessity for using multivariate statistical analytical techniques.

Orthopyroxene is second only to olivine in abundance as a silicate in meteorites. It can be further classified according to its iron content as enstatite, less than 10 mol %  $\text{FeSiO}_3$ ; bronzite, 10-20 mol %  $\text{FeSiO}_3$  and hypersthene, 20-30 mol %  $\text{FeSiO}_3$ . Thus, a prediction can be made on the basis of the linear relations shown in Fig. 2 that bronzite would exhibit a lower thermoluminescence energy density than enstatite, and that hypersthene would exhibit the lowest thermoluminescence emission in the series. Other relatively high Fe pyroxenes, such as pigeonite, would also be expected to exhibit low or no detectable thermoluminescence emission. In view of the high iron concentrations in the lunar pyroxenes, it is not surprising that no significant thermoluminescence emission occurs (for a temperature range of 23-500°C and a heating rate of 80°C/min (Nash, Conel, and Greer, 1970)). The findings emphasize the importance of obtaining detailed chemical

information for single phase material to help understand thermoluminescence response behavior of natural complex materials.

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## CHARACTERIZATION OF NON-LUMINESCENT, NEAR-INSULATING SOLIDS

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Luminescent and semiconducting materials can be characterized in a large number of ways. The detailed interpretation of the measurements may be in doubt from case to case, but there is no shortage of parameters to measure. For near-insulating materials, our experimental repertoire is much smaller, especially if the materials are also non-luminescent, either totally or in the temperature range of interest. This note deals in general and qualitative terms with methods which are thought to have potential uses in such cases.

A procedure which has already been applied to such solids is the measurement of thermally stimulated currents. In the ordinary way, a constant voltage is applied to the specimen and the current monitored while the temperature is being raised at a uniform rate (Bube, 1960) (Fig. 1A). The quantitative interpretation of observed conductances depends on the assumption that significant contact resistances are absent. However, measurement of the temperature ( $T_m$ ) at which the conductance peaks is much less liable to uncertainty. Constant contact resistances, at any rate, should not affect  $T_m$ . This temperature can be used to evaluate a trap activation energy on the basis of various models. The final values must somewhat depend on the detailed nature of these models and will not be highly accurate, but should be sufficiently reliable to serve for comparative and order-of-magnitude orientational purposes.

In practice, the absence of contact resistances or their constancy cannot always be assured. Moreover, the conduction processes in the bulk of the specimen are often space-charge controlled. Both factors lead to voltage-dependent conductances and thus to uncertain values of  $T_m$ . To ascertain whether this is the case, tests for ohmic behavior should always be made. Calculations are in progress which aim at a quantitative

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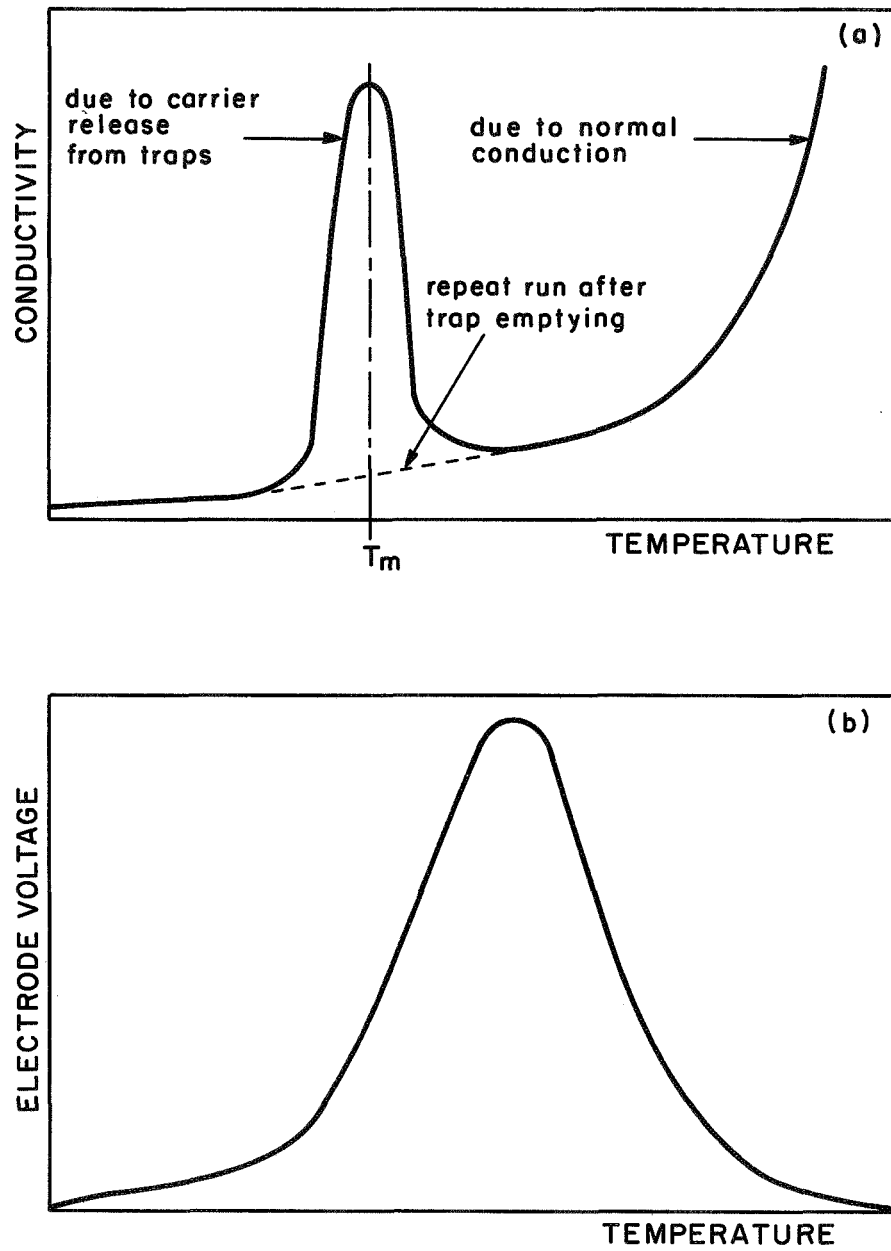


Fig. 1. Trap emptying characteristics: (a) thermally stimulated conductivity, (b) thermo-electret discharge.

assessment of the various sources of error. Another of these arises from the fact that the programmed temperature rise cannot be uniform over the volume of the specimen. Any value of  $T_m$  determined by experiment is therefore, in a sense, an "equivalent temperature," i.e. the result of a more or less complicated averaging process. The correct temperature can, however, be obtained by extrapolating the results to a zero rate of temperature rise. This is essentially equivalent to the standard procedure (Garlick, 1949) for thermoluminescence.

There are alternative procedures which may be applied to materials of even higher (effective) resistivity, which are free from some of the differences associated with non-ohmic behavior; namely electret processes. These regard the material as a medium for polarized charge storage. The amount of charge that can be stored is a measure of the trap density, and the temperature at which the overall dipole is discharged (in the most general terms) is a measure of the trap depth. The method is distinguished from that discussed above, inasmuch as the measurement can be performed without conducting electrodes. Highly insulating layers of small thickness can be interposed between the material under test and the metal electrodes. A thermo-electret is formed by first heating and subsequently cooling the specimen in the presence of a moderately high electric field. The electrodes are temporarily short circuited and then allowed to float. Their potential difference is monitored during a subsequent heating process. This yields a relationship of the type shown in Fig. 1B. An alternative procedure is to form the electret by illumination without heating. The method is capable of yielding a good deal of structure (Zolotarev et al., 1967). It is qualitatively well understood (Fabel and Henisch, 1970) but its quantitative implications remain to be worked out. It represents an approach which is believed to have general merit and application: insulators are often more profitably considered as electrets than simply as poor semiconductors. Figure 2 shows the equipment used in this laboratory.

The detailed interpretation of the trapping centers themselves and, in particular, their identification in crystal-chemical terms is, of course, a different (and equally important) problem. In the most general sense, the concentration of trapping centers is a measure of disorder, which may have implications concerning the processes whereby the material (lunar or otherwise) was originally formed or subsequently treated.

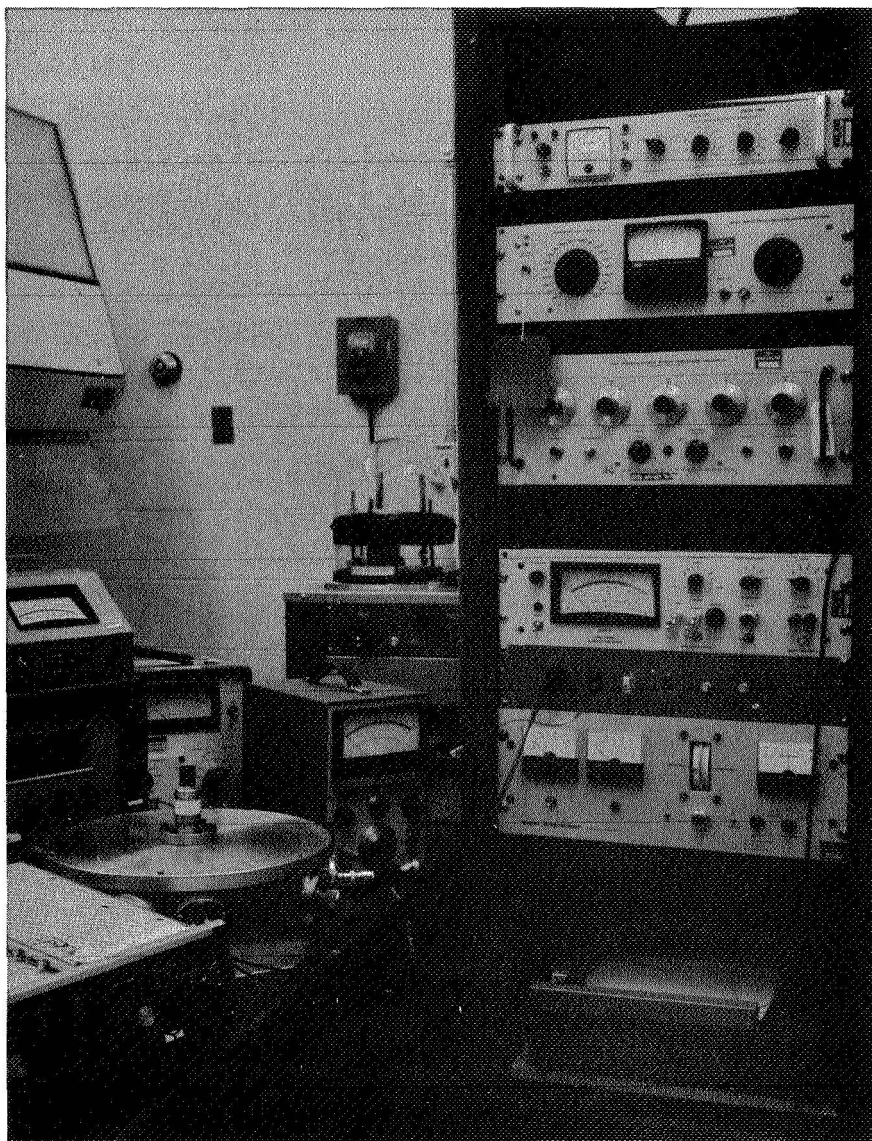


Fig. 2. Equipment employed for electret measurements.

Whereas electret methods are not very precise for diagnostic purposes, they have at this stage no competition from other procedures. On these ground alone further attention to these problems appears justified.

#### Acknowledgement

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## LUMINESCENCE OF OXIDES BY OH ACTIVATION IN HYDROGEN FLAMES

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Candoluminescence is a name applied to luminescence excited by flames--the nonthermal part of the emission of a hot phosphor. In the course of re-examination of this phenomenon we have found efficient low-temperature emission from many rare earth and transition ion doped phosphors. The mechanism of activation is of potential interest to the explanation of transient phenomena on planetary surfaces.

The flame-excited luminescence was obtained by playing a hydrogen diffusion flame over the phosphor surface.  $\text{Tb}^{+++}$ -doped  $\text{Y}_2\text{O}_3$  and  $\text{Lu}_2\text{O}_3$ , as one example, gave a bright green emission.  $\text{Mn}^{++}$ -doped  $\text{Zn}_2\text{SiO}_4$  (willemite) emits a deep green. The spectrum of the rare earth emission is composed of many sharp groups of lines and is characteristic of the rare earth ion. The candoluminescent phosphors are either nonresponsive to photo- and cathodo-activation or have a weaker emission with different colors. The efficiency of the emission is temperature dependent and has a maximum, which, in the case of the  $\text{Tb}^{+++}$ -activated materials is at  $160^\circ\text{C}$ .

Experiments with gases in a microwave discharge show that the luminescence is excited by the discharge from water vapor but not from hydrogen. Indeed, hydrogen quenches the luminescence. It is postulated that the activating species is an excited state of neutral OH.

There is a possible relevance of these results to the interpretation of transient lunar phenomena. An explanation of the TLP in terms of luminescence requires an efficient pumping source--more efficient than any yet available. We suggest the possibility of activated species in the solar plasma or generated on the lunar surface by energetic particle bombardment of surface rocks that could pump the phosphor minerals by the candoluminescence mechanism.

DETAILED CATHODOLUMINESCENCE CHARACTERIZATION  
OF COMMON SILICATES

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INTRODUCTION

Most previous work on cathodoluminescence from minerals has concentrated on studies of their spectral properties, relative efficiencies and distributions of color and intensity with respect to minor element content and variation. Sippel (1966, 1968) observed complex cathodoluminescence patterns in carbonate and quartz mineral grains which revealed petrographic details not observable by other techniques. Most of the applications of cathodoluminescence to mineral studies have been carried out using modified petrographic microscopes where no chemical information can be obtained directly.

The microprobe appears to be a much more suitable tool for cathodoluminescence studies as one achieves high spatial resolution while also being able to determine the microscale chemistry.

For the last few years, part of the research interest at the Materials Research Laboratory has been towards characterization of materials using the phenomenon of cathodoluminescence. The characteristics, which must be measured, include not only spectral colors and intensities but also rise and decay times. The recent awareness that the cathodoluminescence emission is polarized for many materials (Bhalla and White, 1970 a,b) offers additional powerful parameters to study. The directional dependence of polarized emission can give useful information about the site symmetries of the luminescence centers.

For this study a representative suite of minerals has been examined to establish the range of cathodoluminescence characteristics that one might encounter in rock specimens. No attempt was made to explore the range of variation that might be found in a given mineral from several localities.

## EXPERIMENTAL

An Applied Research Laboratory model EMX electron microprobe equipped with simple light spectrometer photomultiplier assembly and a beam pulser was used. Details of the instrumentation and the sample preparation were the same as described by White *et al.* (1970).

Twenty-seven silicates and corundum were prepared as polished thin sections by embedding the crushed minerals in Lakeside 70 and then grinding and polishing. A polished single crystal of  $\text{CaWO}_4$  was used as an arbitrary standard for comparative luminescence efficiency measurements and the efficiency of all the minerals was expressed in percent of  $\text{CaWO}_4$  emission intensity. No correction was made for the variations in the spectral response of the spectrometer and photomultiplier. The probe was operated at 20 keV, and ordinarily with a sample current of  $1 \times 10^{-8}$  amp and a spot diameter of approximately 50 microns. All samples as well as  $\text{CaWO}_4$  were coated with a carbon layer approximately 400 Å thick.

Figure 1 shows the cathodoluminescence data sheet which was developed for recording all the information. The polarization colors were observed with the POLAROID analyzer direction (N) parallel to  $n_\alpha$ ,  $n_\beta$ , or  $n_\gamma$  of the mineral ( $n_e$  or  $n_o$  for the uniaxial minerals). If the optical directions of the minerals were not accurately parallel to  $n_\alpha$ ,  $n_\beta$ , or  $n_\gamma$ , they were marked with a prime.

## RESULTS

The investigated ortho- and ring silicates (Table 1) were mainly non-luminescent. Zircon showed blue and yellow luminescence streaks parallel to the c-axis which were strongly polarized. Olivine (forsterite) had a reddish color with a patchy distribution. The luminescence decayed slowly and was unpolarized. Kyanite was deep red and patchy.

Results for five chain silicates are summarized in Table 2. Jadeite, kunzite and diopside belong to the group of pyroxenes and protoamphibole and grunerite to the hornblende group; kunzite is a lilac colored spodumene of gem quality. Remarkable for kunzite was its longer rise and decay times as well as the high relative efficiency. These characteristics prompted a more detailed study of kunzite (to be reported later).

TABLE 1  
Ortho- and Ring Silicates

MINERAL NAME	CHEMICAL COMPOSITION	CRYSTAL CLASS	CHARACTERIZATION OF CATHODOLUMINESCENCE				
			COLOR	REL. EFFI- CIENCY (IN %)	POLARIZED	POLARIZATION COLORS	RISE TIME IN MS
ZIRCON	Zr [SiO <sub>4</sub> ]	D <sub>4h</sub>	yellow + blue zoned   c	1.2	yes	N  n <sub>e</sub> yellow → intensified blue → black N n <sub>e</sub> yellow → remains blue → gray	0.3
OLIVINE	(Mg,Fe) <sub>2</sub> [SiO <sub>4</sub> ]	D <sub>2h</sub>	reddish slow decay patchy	-	no	-	-
KYANITE	Al <sub>2</sub> [O/SiO <sub>4</sub> ]	C <sub>i</sub>	deep red patchy	0.06	yes, not certain	-	0.1
ANDALUSITE	Al <sub>2</sub> [O/SiO <sub>4</sub> ]	D <sub>2h</sub>	no	-	-	-	-
TOPAZ	Al <sub>2</sub> [Fe <sub>2</sub> /SiO <sub>4</sub> ]	D <sub>2h</sub>	no	-	-	-	-
TITANITE	CaTi [O/SiO <sub>4</sub> ]	C <sub>2h</sub>	no	-	-	-	-
PYROPE	Mg <sub>3</sub> Al <sub>2</sub> [SiO <sub>4</sub> ] <sub>3</sub>	O <sub>h</sub>	no or very weak bluish patchy	-	no	-	-
ALMANDINE	Fe <sub>3</sub> Al <sub>2</sub> [SiO <sub>4</sub> ]	O <sub>h</sub>	no	-	-	-	-
AXINITE	Ca <sub>2</sub> (Mn,Fe)Al <sub>2</sub> BH[SiO <sub>4</sub> ] <sub>4</sub>	C <sub>i</sub>	no	-	-	-	-

TABLE 2  
Chain Silicates

MINERAL NAME	CHEMICAL COMPOSITION	CRYSTAL CLASS	COLOR	REL. EFFI- CIENCY (IN %)	CHARACTERIZATION OF CATHODOLUMINESCENCE			
					POLARIZED	POLARIZATION COLORS	RISE TIME IN MS	DECAY TIME IN MS
ZIRCON	Na Al[Si <sub>2</sub> O <sub>6</sub> ]	C <sub>2h</sub>	wine red rapid decay	-	-	-	0.3	0.3
KUNZITE	Li Al[Si <sub>2</sub> O <sub>6</sub> ]	C <sub>2h</sub>	bright pink	100.00	yes	N   nα' = blue N⊥ nα' = red violet yellow	6	8
DIOPSIDE	Ca Mg[Si <sub>2</sub> O <sub>6</sub> ]	C <sub>2h</sub>	bluish red patchy	0.18	yes	N  c = red N⊥c = blue	0.3	0.3
PROTOAMPHI- BOLE	(Li,Mg) <sub>7</sub> [Si <sub>8</sub> O <sub>22</sub> ]F <sub>2</sub>	C <sub>2h</sub>	reddish patchy	0.04	no	-	0.3	0.3
GRUNERITE	(Fe,Mg) <sub>7</sub> [Si <sub>8</sub> O <sub>22</sub> ](OH) <sub>2</sub>	C <sub>2h</sub>	reddish blue decay to blue	0.05	yes	max. abs.   nβ, no color change	0.3	0.2

Table 3 includes all sheet silicates investigated. Corundum is added for space reasons. All these minerals are luminescent but not polarized. Hectorite showed initial wine red emission which was patchy and faded away rapidly. The decay of this emission could be resolved into two components. The fast component had a decay time of 0.3 ms and the slow component had a decay time of 40 ms. Muscovite also showed initially wine red emission which faded away even more rapidly than that from hectorite. In contrast to hectorite and muscovite the emission color of lepidolite and biotite was blue.

Table 4 contains results for some feldspars. Danburite resembles anorthite, where Al is substituted by boron. The luminescence color of the K-feldspars varies from blue to reddish blue to bluish red, whereas the plagioclases are reddish blue. Except for adularia and danburite all minerals listed in Table 4 gave polarized emission for  $N \parallel n\alpha$  blue, for  $N \perp n\alpha$  red. Microcline and oligoclase showed no color change, only a change of the intensity, whereas anorthite showed different colors. It may be noted that the rise and decay times (between 0.1 and 0.3 ms) for all the minerals in this class are similar to most of the other silicates studied.

#### SUMMARY

A scheme for the detailed cathodoluminescence characterization of minerals has been developed. Important features recorded were: 1) color of emission, 2) intensity and intensity variations, 3) change with exposure to the electron beam, 4) polarization properties, and 5) rise and decay times. The predominant cathodoluminescence colors were red and blue.

The relative efficiencies of most of the samples studied were on the order of 2% or smaller and the rise and decay times follow at a constant value of around 0.2 - 0.3 ms. It is assumed that this similar behavior of all these minerals (except kunzite and corundum) is due to the intrinsic luminescence, characteristics of the  $SiO_4$  groups. Only kunzite differed markedly from the other described minerals. The longer rise and decay times are on the same order as for willemite ( $Zn_2SiO_4 - Mn^{2+}$ ) and the relative efficiency is comparable to that of  $CaWO_4$ . It is assumed that  $Mn^{2+}$ , in the octahedral sites in kunzite, is responsible for the pink luminescence.

TABLE 3  
Sheet Silicates + Corundum

MINERAL NAME	CHEMICAL COMPOSITION	CRYSTAL CLASS	CHARACTERIZATION OF CATHODOLUMINESCENCE					
			REL. EFFI- CIENCY (IN %)	POLARIZED	POLARIZATION COLORS	RISE TIME IN MS	DECAY TIME IN MS	
HECTORITE	Na <sub>0.33</sub> (Mg <sub>2.67</sub> Li <sub>0.33</sub> ) [OH] <sub>2</sub> /Si <sub>4</sub> O <sub>10</sub> ]	C <sub>2h</sub>	wine red rapid decay patchy	0.05	no	-	fast comp. 0.2 slow comp. 40.0	0.3 40.0
MUSCOVITE	K Al <sub>2</sub> [(OH,F) <sub>2</sub> / AlSi <sub>2</sub> O <sub>10</sub> ]	C <sub>2h</sub>	wine red to black rapid	-	no	-	-	-
LEPIDOLITE	K (Li,Al) <sub>3</sub> [F,OH,O) <sub>2</sub> / AlSi <sub>3</sub> O <sub>10</sub> ]	C <sub>2h</sub>	weak blue	0.09	no	-	0.2	0.3
BIOTITE	K (Mg, Fe, Mn) <sub>3</sub> [(OH,F) <sub>2</sub> / AlSi <sub>3</sub> O <sub>10</sub> ]	C <sub>2h</sub>	blue slow decay	1.8	no	-	0.2	0.3
CORUNDUM	α-Al <sub>2</sub> O <sub>3</sub>	D <sub>3d</sub>	blue	0.1	no	-	0.2	0.3

TABLE 4  
Framework Silicates

MINERAL NAME	CHEMICAL COMPOSITION	CRYSTAL CLASS	COLOR	REL. EFFI- CIENCY (IN %)	CHARACTERIZATION OF CATHODOLUMINESCENCE			
					POLARIZED	POLARIZATION COLORS	RISE TIME IN MS	DECAY TIME IN MS
ADULARIA	K[AlSi <sub>3</sub> O <sub>8</sub> ]	C <sub>2h</sub>	blue	0.18	no	-	0.2	0.3
ORTHOCLASE	K[AlSi <sub>3</sub> O <sub>8</sub> ]	C <sub>2h</sub>	reddish blue	0.15	yes	N  n <sub>α</sub> =blue N⊥n <sub>α</sub> =red	0.3	0.2
ORTHOCLASE	K[AlSi <sub>3</sub> O <sub>8</sub> ]	C <sub>2h</sub>	bluish red patchy	0.11	yes	N  n <sub>α</sub> '=blue N⊥n <sub>α</sub> '=red	0.2	0.3
MICROCLINE	K[AlSi <sub>3</sub> O <sub>8</sub> ]	C <sub>i</sub>	strong blue patchy	0.75	slightly	N  n <sub>α</sub> '=min. N⊥n <sub>α</sub> '=max. intensity	0.1	0.3
OLIGOCLASE	10 - 30% An	C <sub>i</sub>	reddish blue patchy	0.22	yes	N  n <sub>α</sub> '=min. N⊥n <sub>α</sub> '=max. intensity	0.3	0.3
ANDESINE	30 - 50% An	C <sub>i</sub>	reddish blue	0.50	yes	N  n <sub>α</sub> '=blue N⊥n <sub>α</sub> '=red	0.3	0.3
LABRADORITE	50 - 70% An	C <sub>i</sub>	reddish blue	0.30	yes	N  n <sub>α</sub> '=blue N⊥n <sub>α</sub> '=red	0.2	0.3
ANORTHITE	90 -100% An	C <sub>i</sub>	reddish blue	0.06	yes	N  n <sub>α</sub> '=grey N⊥n <sub>α</sub> '=reddish blue	0.2	0.3
DANBURITE	Ca[B <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> ]	D <sub>2h</sub>	bright blue	0.57	no	-	0.2	0.3



### Acknowledgment

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# CATHODOLUMINESCENCE DATA SHEET

1. Date \_\_\_\_\_ 5. Condition of Sample \_\_\_\_\_
2. Operator \_\_\_\_\_ 6. Accelerating Voltage \_\_\_\_\_ keV
3. Sample No. \_\_\_\_\_ 7. Spot Diameter \_\_\_\_\_
4. Mineral Name \_\_\_\_\_
8. Sample is luminescent (circle one):      Yes              No              Color: \_\_\_\_\_
9. If yes, how does luminescence change with time: \_\_\_\_\_
- \_\_\_\_\_ No change
- \_\_\_\_\_ Color change
- \_\_\_\_\_ Rapid decay
- \_\_\_\_\_ Intensity increases
- \_\_\_\_\_ Initially no lum.
- \_\_\_\_\_ Other (explain) \_\_\_\_\_
10. Distribution of Luminescence: \_\_\_\_\_
- \_\_\_\_\_ Uniform
- \_\_\_\_\_ Patchy
- \_\_\_\_\_ Zoned
- \_\_\_\_\_ Streaked
- \_\_\_\_\_ Color Range
- \_\_\_\_\_ Other (explain) \_\_\_\_\_
11. Relative Efficiency (without monochromator):  
(normalized specimen current)      Sample \_\_\_\_\_ V    at \_\_\_\_\_  $\mu$ A S.C.  
CaWo<sub>4</sub> \_\_\_\_\_ V    at \_\_\_\_\_  $\mu$ A S.C. \_\_\_\_\_ %
12. Luminescence is Polarized (circle one):      Yes              No
13. If yes:      Orientation              Polarization Colors
- N || n <sub>$\alpha$</sub>  or n<sub>e</sub>              \_\_\_\_\_
- N || n <sub>$\beta$</sub>               \_\_\_\_\_
- N || n <sub>$\gamma$</sub>  or n<sub>o</sub>              \_\_\_\_\_
14. Rise Time \_\_\_\_\_ ms
- Decay Time \_\_\_\_\_ ms

Figure 1 '

# INTRINSIC CATHODOLUMINESCENCE EMISSION FROM WILLEMITE SINGLE CRYSTALS

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## INTRODUCTION

It has been known for some time that various unactivated silicates fluoresce when excited by x-rays or cathode-rays (Leverenz, 1950). Similarly, various tungstates and vanadates are also known to fluoresce with moderate efficiencies without any incorporated foreign activators (Walter and Butler, 1969). Emission spectra of the vanadates and tungstates which are also excited by ultraviolet cannot be explained by optical transitions within the  $W^{6+}$  or  $V^{5+}$  ions, as the energy needed for excitation would fall deep in the vacuum ultraviolet. Thus, it was recognized very early (Kroger, 1948) that this intrinsic luminescence must be ascribed to the whole of the  $(SiO_4)^{4-}$ ,  $(WO_4)^{2-}$  or  $(VO_4)^{3-}$  complexes rather than to the cation alone.

In this paper a detailed study of the intrinsic cathodoluminescence emission from oriented willemite single crystals, including directional dependence of polarization, is described. Explanation of the results is attempted on the basis of molecular orbital theory and symmetry arguments.

## EXPERIMENTAL

Natural willemite single crystals from Tsumeb, Southwest Africa were used in this study. Electron microprobe analysis showed them to be free of Fe and Mn impurities. These crystals show only weak pale violet-blue cathodoluminescence, which is characteristic of pure willemite ( $Zn_2SiO_4$ ). It is often mentioned in the literature (Leverenz, 1950) that excess of silica might be necessary to obtain efficient intrinsic luminescence. Thus, it was felt that it may be necessary to introduce a slight excess of silica in the available willemite crystals. This was attempted by vacuum evaporating a thin layer (100–200Å) of  $SiO_2$  onto the polished crystal surfaces and then heat treating for a few hours at 1250°C. This treatment did result in

increased efficiency of emission. However, it was found that even simple heat treatment at 1250°C, without any evaporated  $\text{SiO}_2$  layer, also results in an increase of the luminescence efficiency. The possibility exists that Zn is volatilized by the heat treatment and that this also is a mechanism for effectively enriching the  $\text{SiO}_2$  content.

Sample preparation and experimental setup using the electron microprobe were as described previously (Bhalla and White, 1970).

#### EXPERIMENTAL RESULTS AND DISCUSSIONS

Crystals oriented such that the  $\underline{c}$ -axis of willemite (referred to hexagonal axes) was perpendicular to the surface show characteristic pale violet-blue cathodoluminescence which is not polarized. However, crystals oriented such that the crystal surface contained the  $\underline{c}$ -axis showed strong polarization of the emitted luminescence. The electric vector of the emission was found to be parallel to the  $\underline{c}$ -axis. Angular dependence of polarization,  $p(\theta)$ , (refer to Bhalla and White, 1970), is shown in Figure 1. The degree of polarization,  $p$ , was found to be 0.75. It was not possible to record a complete spectrum of this emission with the spectrometer attachment used in this study as the cut-off of the instrument is at about 4080Å and the peak position of the broad band seemed to fall just beyond this limit. However, there was no visually detectable color change of the emitted luminescence for the two polarization directions.

The willemite structure was determined by Bragg and Zachariasen (1930). Both  $\text{Zn}^{2+}$  atoms and  $\text{Si}^{4+}$  are four-fold coordinated, forming approximately tetrahedral arrangements.  $\text{SiO}_4$  tetrahedra do not share any oxygens, thus they exist as isolated groups in this structure. Two of the Si-O bonds in each  $\text{SiO}_4$  group are oriented in the basal plane and the other two bonds are oriented on a plane containing the  $\underline{c}$ -axis.

As stated earlier, the pale violet-blue emission of pure willemite has been thought to involve the entire  $\text{SiO}_4$  tetrahedral group or molecule. Simple crystal field theory cannot be applied for this case as the Si-O bonds have considerable covalent character, making it necessary to introduce the more complicated molecular orbital treatment to explain the spectra. Recently, Walter and Butler (1969) carried out semi-empirical LCAO-MO (Linear Combination of Atomic Orbitals-Molecular Orbital) calculations on

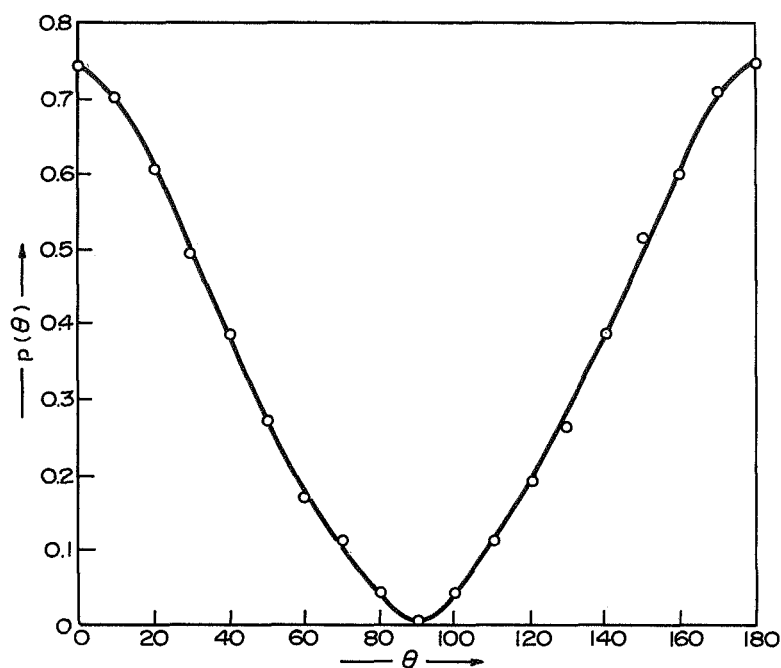


Fig. 1. Polarization  $p(\theta)$  and angle  $\theta$ , measured between the  $c$ -axis and the analyzer direction.  $p(\theta) = (I_\theta - I') / (I' + I'')$ , where  $I'$  and  $I''$  are maximum and minimum intensities measured as the analyzer is rotated around its axis.

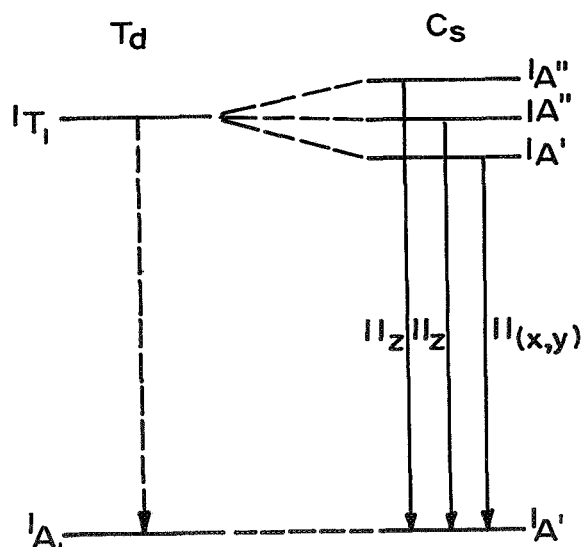


Fig. 2. Splitting of triply degenerate level  ${}^1T_1$  under the reduced symmetry  $C_s$ . The  $T_d$  transition  ${}^1T_1 \rightarrow {}^1A_1$  is forbidden, but under the reduced symmetry  $C_s$ , the two transitions  ${}^1A'' \rightarrow {}^1A'$  are allowed in the  $z$ -direction and the transition  ${}^1A' \rightarrow {}^1A'$  is allowed in the  $(x,y)$  directions by electric-dipole selection rules.

the tetrahedral  $(VO_4)^{3-}$  and  $(WO_4)^{2-}$  complexes. Since these are isoelectronic with the  $(SiO_4)^{4-}$  complex, similar energy level diagrams, differing only in relative energy, can be expected for  $(SiO_4)^{4-}$  also. According to Walter and Butler the emission transition for such complexes is  $2e \rightarrow t_1$ . The ground state configuration is  $(t_1)^6$ , which results in a singlet term,  $^1A_1$ . The excited state, with configuration  $(t_1)^5(2e)$ , splits up into multiplets  $^1T_1$ ,  $^1T_2$ ,  $^3T_1$  and  $^3T_2$  when the effect of electrostatic repulsion of electrons is also taken into account (Walter and Butler, 1969). Symmetry considerations show that for perfect Td complexes, the only electric-dipole allowed transitions to the ground level  $^1A_1$  would be from levels with  $T_2$  symmetry. Transitions from  $T_1$  levels are forbidden. However, any lowering of symmetry would split the triply degenerate  $T_1$  levels and the transitions would then be allowed. The order of levels is not certain. Walter and Butler (1969) put either  $^3T_1$  (for  $CaWO_4$ ) or  $^1T_1$  (for  $YVO_4$ ) as the lowest level. Since the ground state is a singlet, a transition from the triplet state is allowed only to the extent that there is spin-orbit coupling, which is very small for  $(SiO_4)^{4-}$ . It is not certain which level is the emitting (lowest) level for  $Zn_2SiO_4$  but most likely it is  $^1T_1$ . However, even if  $^3T_1$  is taken as the emitting level, the same results would be obtained as far as polarization under the reduced symmetry is concerned, since for group theoretical arguments, only the symmetry of the levels is important.

The space group symmetry of the  $SiO_4$  group in willemite is  $C_1$  (Bragg and Zachariasen, 1930); however, the mere fact that the luminescence is polarized leads to the conclusion that the emitting center has a higher symmetry than  $C_1$ . At the same time, the symmetry is lower than that of perfect Td, since for Td symmetry also, no polarization would be expected. Also, the transition from  $T_1$  levels are forbidden for Td. In an effort to find distortions in  $SiO_4$  tetrahedron, various bond lengths were calculated from the Bragg and Zachariasen (1930) structure (Table 1). As can be seen from this table the distortions are not large enough to assign any significantly reduced symmetry on this basis. Also, as the refined atomic coordinates for  $Zn_2SiO_4$  are not available, it is not safe to assign symmetry from such small variations in bond lengths. Attempts were made to explain

TABLE 1

Various Bond Lengths around Distorted  $\text{SiO}_4$  Tetrahedron

Bond Type	Bond Length (Å)
Si - O <sub>1</sub>	1.74
Si - O <sub>2</sub>	1.72
Si - O <sub>3</sub>	1.72
Si - O <sub>4</sub>	1.76
O <sub>1</sub> - O <sub>2</sub>	2.77
O <sub>1</sub> - O <sub>3</sub>	2.83
O <sub>1</sub> - O <sub>4</sub>	2.91
O <sub>2</sub> - O <sub>3</sub>	2.83
O <sub>2</sub> - O <sub>4</sub>	2.85
O <sub>3</sub> - O <sub>4</sub>	2.83

the observed polarization solely by considering various possible lower symmetries and working out selection rules for these symmetries using group theoretical arguments. These considerations show that the observed polarization can be best explained by assigning  $C_s$  pseudo-symmetry to the  $\text{SiO}_4$  group. The symmetry axis (z-axis) would be along the crystallographic c-axis. Under  $C_s$  symmetry the  $^1T_1$  level would split up into three levels (Figure 2). Two of these would have  $A''$  symmetry and the third  $A'$ . Transitions from two  $^1A''$  levels to the ground  $^1A'$  level are allowed in the z-direction and the transition  $^1A' \rightarrow ^1A'$  is allowed in (x,y) directions. Thus we would expect partial polarization along the crystallographic c-axis of willemite. The magnitude of observed polarization, however, is greater than the expected value.

It may be pointed out here that only electric-dipole type transitions were considered to explain the observed polarization.

#### SELECTION RULES FOR VARIOUS LOWER SYMMETRIES

For the interpretations of the polarized emission from distorted tetrahedral  $(\text{SiO}_4)^{4-}$  groups in the silicates (or other isoelectronic complexes as  $(\text{WO}_4)^{2-}$  or  $(\text{VO}_4)^{3-}$  it is necessary to calculate selection rules under the reduced symmetry conditions. Such calculations were carried out for various possible lower symmetries for the transitions  $T_1 \rightarrow A_1$  and  $T_2 \rightarrow A_2$ . The results are tabulated in Tables 2 and 3.

TABLE 2

Selection Rules under Reduced Symmetry Conditions  
for the Emission Transition  $T_2 \rightarrow A_1$   
(A = Allowed; F = Forbidden)

REDUCED SYMMETRY OF THE MOLECULE	SPLITTING OF "Td" LEVEL $T_1$	POLARIZATION OF EMITTED RADIATION		
		x	y	z
$D_{2d}$	E	A	A	F
	$A_2$	F	F	F
$C_{3v}$	E	A	A	F
	$A_2$	F	F	F
$S_4$	E	A	A	F
	A	F	F	F
$D_2$	$B_1$	F	F	A
	$B_2$	F	A	F
	$B_3$	A	F	F
$C_{2v}$	A	F	F	F
	$B_1$	A	F	F
	$B_2$	F	A	F
$C_3$	E	A	A	F
	A	F	F	A
$C_2$	A	F	F	A
	B	A	A	F
	B	A	A	F
$C_s$	$A'$	A	A	F
	$A''$	F	F	A
	$A'''$	F	F	A



TABLE 3  
Selection Rules under Reduced Symmetry Conditions  
for the Emission Transition  $T_2 \rightarrow A_1$   
(A = Allowed; F = Forbidden)

REDUCED SYMMETRY OF THE MOLECULE	SPLITTING OF "Td" LEVEL $T_2$	POLARIZATION OF EMITTED RADIATION		
		x	y	z
$D_{2d}$	E	A	A	F
	$B_2$	F	F	A
$C_{3v}$	E	A	A	F
	$A_1$	F	F	A
$S_4$	E	A	A	F
	B	F	F	A
$D_2$	$B_1$	F	F	A
	$B_2$	F	A	F
	$B_3$	A	F	F
$C_{2v}$	$A_1$	F	F	A
	$B_1$	A	F	F
	$B_2$	F	A	F
$C_3$	A	A	A	F
	E	F	F	A
$C_2$	A	F	F	A
	B	A	A	F
	B	A	A	F
$C_s$	$A'$	A	A	F
	$A''$	A	A	F
	$A'''$	F	F	A

#### SUMMARY

Intrinsic cathodoluminescence emission from oriented willemite ( $Zn_2SiO_4$ ) single crystals was studied using an electron microprobe. Natural willemite crystals, free of manganese and iron impurities, were used. The emission was found to be strongly polarized for the crystals oriented such that the  $\underline{c}$ -axis was in the surface. The electric vector of emission was along the  $\underline{c}$ -axis and the degree of polarization was 0.75. Crystals with orientation such that the  $\underline{c}$ -axis was perpendicular to the surface did not show any polarization.

This intrinsic emission cannot be explained by considering transitions within the  $\text{Si}^{4+}$  ion and whole of  $(\text{SiO}_4)^{4-}$  tetrahedral complex has to be considered. Molecular orbital theory and symmetry arguments were used to explain anisotropy of emission from  $(\text{SiO}_4)^{4-}$  complex. These arguments led to the conclusion that the symmetry of the  $(\text{SiO}_4)^{4-}$  tetrahedra is reduced to  $C_s$  in willemite. Selection rules for various possible lower symmetries of  $(\text{SiO}_4)^{4-}$  type of molecular orbital complexes were also calculated as an aid for the interpretation of polarized luminescence from such molecules in solids.

#### Acknowledgments

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THE LUMINOSCOPE - A NEW INSTRUMENT FOR STUDYING THE  
ELECTRON-STIMULATED LUMINESCENCE OF TERRESTRIAL,  
EXTRA-TERRESTRIAL AND SYNTHETIC MATERIALS  
UNDER THE MICROSCOPE

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ABSTRACT

Cathodoluminescence microscopy promises to become an important instrumental technique in mineralogy, petrology and other disciplines, since electron luminescence very often clearly reveals features which are not detectable by ordinary petrographic techniques.

An inexpensive device designed to facilitate studies of the cathodoluminescence of minerals and other materials that results from bombarding a specimen in a vacuum chamber with energetic electrons is described. This apparatus, the Luminoscope, permits observations to be made at magnifications up to 800 using standard microscopes. The beam can be adjusted to illuminate specimen areas from 0.5 mm to 50 mm in diameter with a beam of electrons having energies up to 18,000 volts at currents of up to 0.5 mA. Thin and thick sections as well as irregularly shaped specimens and grains can be studied.

Examples of applications are given, including: monitoring mineral separations, distinguishing between sedimentary and detrital igneous quartz, detecting radioactive impurities in quartz, differentiating between Na- and K-rich phases of perthitic intergrowths, studying the distribution of calcitic cement in sandstones and shales, understanding the dolomitization process, revealing the former presence of shells and other fossil materials in recrystallized limestones, studying the luminescence of serpentines, estimating the extent of equilibration of chondrites, studying shock-disordering of plagioclase in lunar rocks, determining the degree of perfection of synthetic mineral crystals, studying oxidation/reduction in flame-grown crystals, "fingerprinting" gems, and tracing the origin of prehistoric pottery.

## INTRODUCTION

Cathodoluminescence or electron stimulated luminescence is fast becoming an important petrological tool, and promises to be applicable routinely to a wide range of research problems in other fields also. Many types of information unobtainable with ordinary petrographic techniques are clearly revealed by the cathodoluminescence of mineral samples.

Features such as compositional zoning, fracture filling, exsolution, inter-growths, recrystallization, attainment of equilibrium, skeletal structures, radiation halos, and certain types of organic remains, which either cannot be detected by conventional petrological techniques, or can only be studied by tedious experiments, are in many cases very obvious when the specimen is bombarded by electrons in a vacuum, since both the color and intensity of luminescence are dependent upon very small changes in the concentrations of trace impurities, as well as on the matrix substances and the way in which impurities are incorporated in the base material.

Pioneers in the use of luminescence as a petrologic technique in the 1960's included J. V. Smith of Chicago (Stenstrom and Smith, 1964; Smith and Stenstrom, 1965), J. V. P. Long and S. O. Agrell of Cambridge (Long, 1963; Long and Agrell, 1965), and R. F. Sippel of Mobil Oil (Sippel and Glover, 1965; Sippel, 1968). Although the phenomenon has been known since early in the century and vacuum-tube demonstrations of cathodoluminescence have been on display in numerous museums for many years, the "modern" period of development of luminescence microscopy perhaps only began in 1963 with papers of Smith and Long. The renewal of interest in the technique at this time was a consequence of the development of the electron-bombardment-stimulated x-ray microprobe in the 1950's and 60's, with which luminescence was commonly observed as a byproduct of studies undertaken for other purposes.

## DESCRIPTION OF LUMINOSCOPE

In 1965, at the suggestion of Prof. Smith, Nuclide began development of an inexpensive device that could be attached to an ordinary microscope for observing a specimen under bombardment by electrons having energies of up to about 20,000 volts. The resulting instrument, which we have called the "Luminoscope"<sup>R</sup>, consists essentially of a variable high voltage power supply, and a vacuum chamber with attached electron gun, mounted on the microscope stage, the unit being engineered to provide maximum safety from high voltages

and x-rays and operating ease. In contrast to the microprobe, such an instrument can be sold for a few thousand dollars.

Since its introduction, the instrument has been improved markedly as to convenience of sample introduction, the precision of its motions, the maximum useable magnification, and especially, the maximum intensity achievable, and hence, the speed with which luminescence could be recorded photographically. Also, some useful accessories have been introduced. The latest version, model ELM-2A, is shown in Figure 1. The power supply is at the left and the vacuum chamber at the right, mounted in position for use on the stage of a simple metallographic microscope.

Figure 2 shows details of the vacuum chamber in plan and elevation. With the standard vacuum window arrangement shown, magnifications of up to 200 can be used conveniently. However, magnifications as high as 600-800 can now be used by installing a recessed window accessory (introduced this year) in place of the upper window; with this, working distance can be as low as five millimeters.

The specimen is traversed on a two-axis motion device inside the vacuum chamber, under the electron beam. The tolerances on the present motion mechanism are such that specimens will remain in focus at magnifications up to 800X, and at magnifications approaching this motion appears smooth and jerk-free.

The Luminoscope's vacuum chamber is arranged so that either thin or thick sections, loose grains, or even, irregular bulk samples can be studied. (For the standard chamber maximum specimen size is 2x3x1/2 inches.) Windows are provided on both sides of the chamber so that conventional petrographic observations can be made on specimens without breaking vacuum or repositioning. When the electron beam is switched "off" an electrical outlet to which a microscope illuminator can be attached is automatically switched "on".

Another convenience feature in the ELM-2A is the e-beam deflection assembly (see Fig. 2). In earlier models the electron gun was mounted at an angle to the horizontal so that the electrons of the beam would strike the specimen at an angle of 15 degrees. This caused space problems in using the chamber with some microscopes. In the ELM-2A, however, the gun is horizontal and produces a horizontally-directed beam which is deflected onto the surface by the permanent magnets of the deflection assembly. By moving this assembly one can also change the location on which the beam impacts. Very recently, we have also added a means of focusing the electron beam. This is conveniently

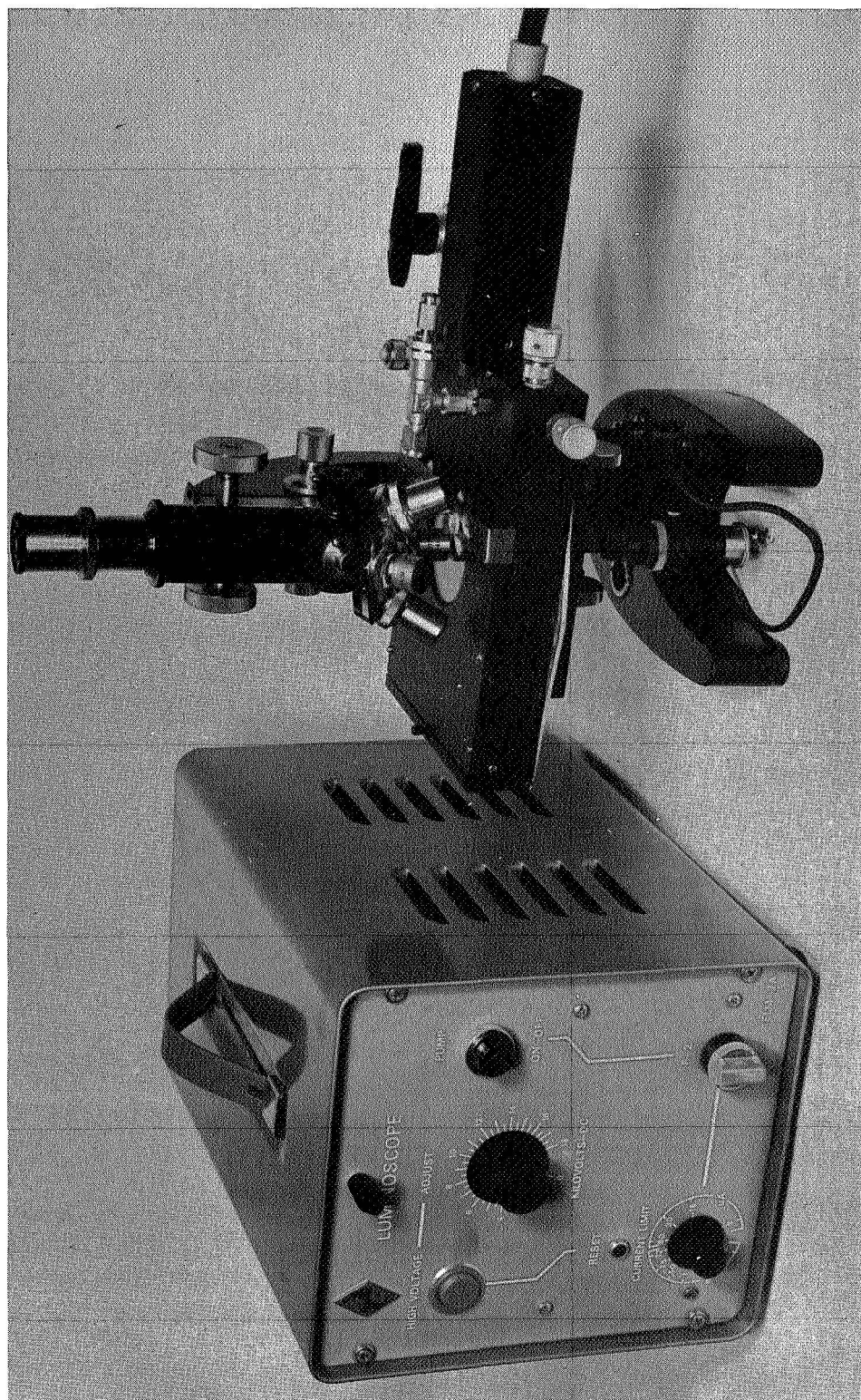


Fig. 1. The "third generation" Luminoscope, Model ELM 2A, with specimen chamber installed on stage of Unitron metallographic microscope. (Vacuum pump not shown.)

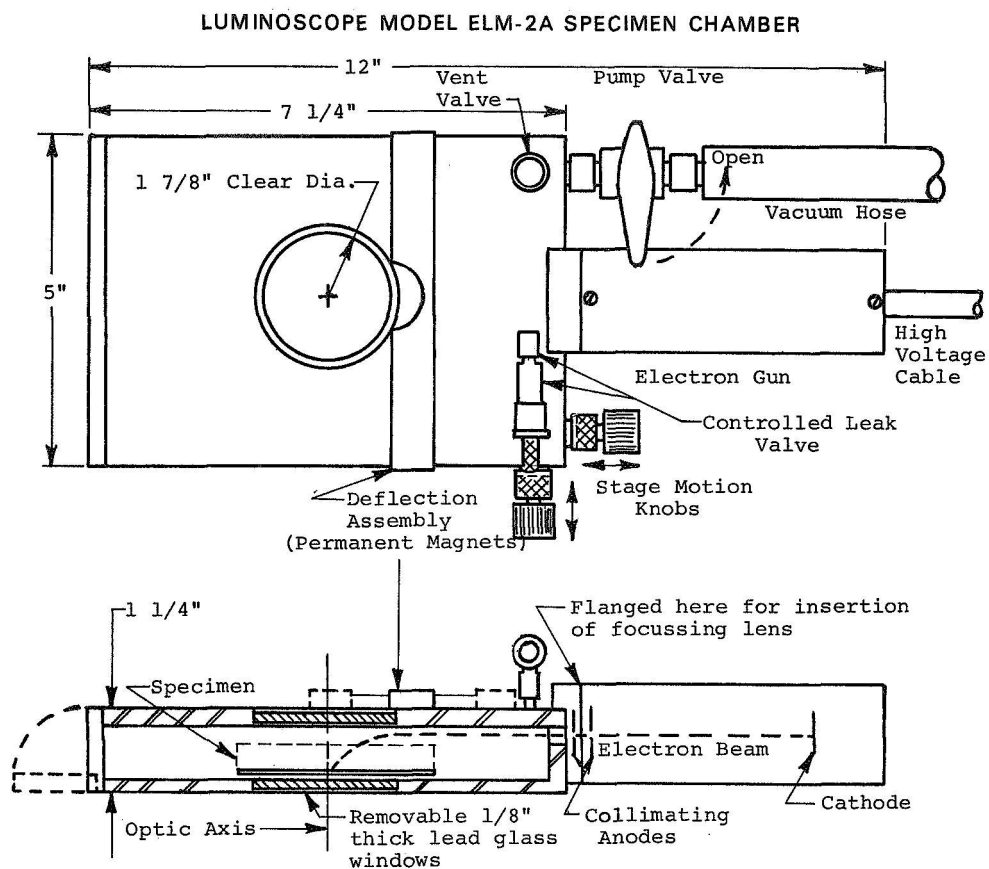


Fig. 2. Specimen chamber of ELM 2A Luminoscope, showing features (plan and section).

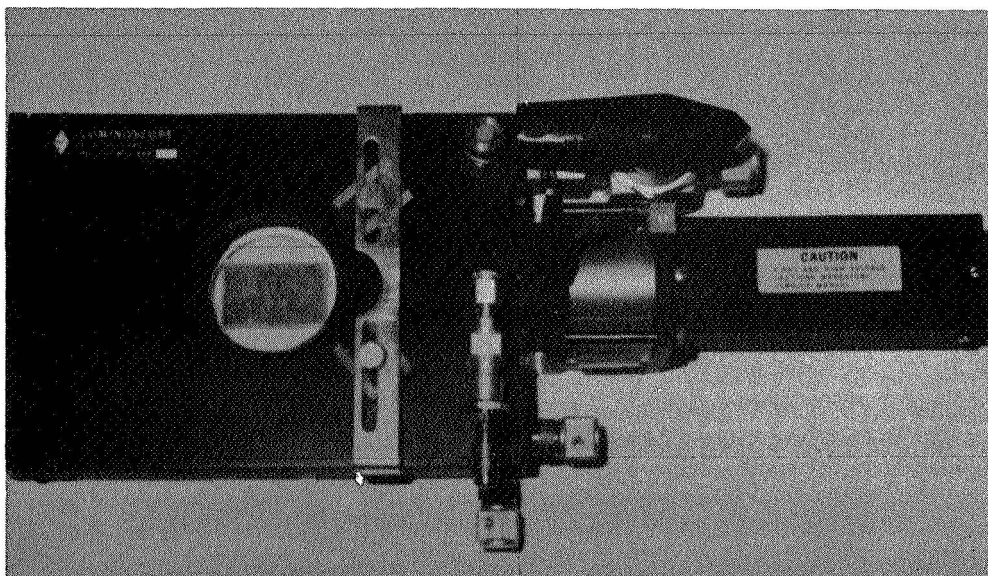


Fig. 3. Electromagnetic focusing coil installed on electron gun of ELM-2A Luminoscope.

accomplished by means of an accessory electromagnetic focusing coil, shown in place on the gun in Figure 3. This makes it possible to concentrate the beam current into a spot about one-half millimeter in diameter. Alternatively, it can be used to defocus the spot to diameters of 2" or greater.

The limits of travel of the internal specimen-translation stage are approximately 2 and 3 inches in the two directions parallel to the microscope stage.

The specimen chamber mounts directly onto fixed or rotatable microscope stages. It can also be used without a microscope.

For safety in servicing the unit, all high voltages are isolated by an automatic relay. The high voltage also turns off automatically if the beam current becomes too great.

In the present Luminoscope (in contrast to the original version which used an a.c. power supply), only electrons bombard the specimen surface. These are produced in a "cold cathode" discharge.

The cold cathode was chosen as the electron source because of the following advantages it offers:

1. A cold cathode electron gun operates at mechanical pump pressures, so that the vacuum system required is not complex and operating pressure is easy to achieve after opening the chamber.
2. Filament burnout cannot occur, and only occasional cleaning is necessary.
3. Depositing a conductive coating on the sample (as is necessary in the electron microprobe) is generally not required, since at these operating pressures, the charge brought by impacting electrons is rapidly removed by gas molecules colliding with the specimen.
4. The electron current obtained from a cold cathode discharge at a given voltage varies directly with the pressure. In the present Luminoscope, for example, at a pressure of a few microns (attained in about 3 minutes of pumping) a beam current of about one-half milliamp is obtained when the D.C. voltage is at its maximum of 18,000 volts.

Since the "bottoming" pressures of good mechanical pumps are too low to maintain a glow discharge, air or some other gas such as helium must be admitted to the chamber to keep the discharge going. In the Luminoscope, a variable leak valve is provided for this purpose. Changing the composition of this gas provides another useful technique for studying surfaces.



## SOME APPLICATIONS OF ELECTRON LUMINESCENCE PETROLOGY AND MINERALOGY

There are now approximately fifty Luminoscopes in service, most of them being of first or second generation design, and their applications cover many fields. A few of these will now be described, including, in keeping with the theme of this Symposium, studies of meteorites and lunar rocks. However, most of the specimens studied thus far have been terrestrial rocks, and so most of the illustrations of the applicability of luminescence to petrology and mineralogy will be taken from such studies. Some of the photos were made using an electron microprobe. In the making of these, the magnification used was always 268X and exposure times were in the range 10 to 25 minutes. In contrast, for the Luminoscope slides, because of the greater intensity of the beam, exposure times are 12 to 24 seconds, and magnifications are 50X except as noted.

### Separating Minerals

A cathodo-luminescence microscope is a useful tool for monitoring the progress of mineral separation procedures.

An application of interest to this audience was made by R. Van Schnuss of the Air Force laboratory in Bedford, Mass., working with one of the authors (D.J.M.) in studies of meteorites from which pure mineral samples had been separated. Chondritic phosphates (merrillite) and feldspar grain separates were viewed periodically with the Luminoscope. The phosphates had a distinct orange luminescence while the feldspar luminescence was light blue. Little difficulty was experienced in "spotting" single grains of either mineral in an otherwise pure sample of the other.

Similarly, in a three-component mixture of calcite, quartz, and orthoclase, ordinarily each mineral luminesces quite differently--for example, calcite, reddish orange; feldspar, blue; and quartz, light blue to almost non-luminescent. When there is a grain of one of these three components in a supposedly pure mineral aggregate of one of the others, it can be identified easily. This provides a convenient way to check on the purity of grain samples, especially after storage.

Of course this technique for monitoring mineral separations will only be effective if the differences in luminescence are sufficient to permit identification of each mineral. If this is true, generally a total time of only 2 to 3 minutes is required to take a sample, place it in the Luminoscope, and make the observation, if the grains are dry. The sample (except for its surface)

is not modified in any manner by the observation, so it can be returned to the separative device afterwards.

### Quartz and silica

Euhedral (in ordinary light) quartz grains in a partially dolomitized limestone were observed by Smith and Stenstrom (1965) under electron bombardment. It was discovered that these grains typically consisted of two parts--the center portions were rounded grains (bright blue) surrounded by regions of entirely different luminescent characteristics--dull red to black. Fig. 4 shows one such grain in an orange-luminescing matrix of calcite. The luminescence difference was attributed to the fact that the cores consisted of detrital quartz formed at elevated temperature while the overgrowth consisted of more pure low-temperature silica that grew in the sediment. Some of these crystals showed in ordinary light a line of dust particles or other imperfections from which one could deduce that there were two regions, but others did not and the fact there were two stages was only revealed by luminescence. Fig. 4 also shows a red dolomite rhomb with an iron-bearing rim (black).

In a sandstone studied by Smith and Stenstrom (1965) the outlines of the detrital quartz grains are difficult to see in ordinary light. They are much more readily visible in luminescence (Fig. 5). The primary quartz shows bright blue luminescence, while the quartz cement which fills most of the space between the grain shows a dull red luminescence. Since the cement grows in optical continuity with the primary grains, the boundary cannot be detected by change of extinction angle. (The black material in the photo is not quartz--possibly it is a clay mineral.)

Likewise, Sippel (1968) studying a "pressure-formed" sandstone, found that many grains actually consisted of rounded centers (glowing blue) surrounded by secondary quartz that was almost nonluminescent. This had grown in such a way as to be responsible for many of the features attributed by earlier investigators to "pressure" when they studied the rock in ordinary light. Such information on the true state of affairs is of course of critical value to persons studying sedimentary rocks, and is often easily obtained through luminescence microscopy.

Smith has also shown that luminescence can sometimes be used to reveal the distribution of alpha-radioactive impurities. He observed circular areas of reddish luminescence in quartz crystals (the quartz luminescing in the blue). Conventional microscopy showed no reason for this, but microprobe scans

- Fig. 4. Cathodoluminescence of quartz crystal in limestone (Microprobe, 20KV, 0.4  $\mu$ a, 10 min., X268).
- Fig. 5. Cathodoluminescence of detrital quartz grains showing filling between grains by purer deposited quartz and carbonaceous material. (Microprobe, 25KV, 0.5  $\mu$ a, 8 min., X268).
- Fig. 6. Cathodoluminescence of microcline perthite showing albite vein in K-rich region. (Microprobe, 20KV, 0.15  $\mu$ a, 23 min., X268).
- Fig. 7. Cathodoluminescence of perthite consisting of albite and K-feldspar. (Microprobe, 20KV, 0.3  $\mu$ a, 15 min., X268).
- Fig. 8. Cathodoluminescence of hematite in feldspar. (Microprobe, 20KV, 0.15  $\mu$ a, 20 min., X268).
- Fig. 9. Cathodoluminescence of calcitic siltstone; calcitic cement is orange red (ELM 2 Luminoscope, X50).
- Fig. 10. Cathodoluminescence of dolomite growing in calcite matrix showing black Fe-rich borders of dolomite rhombs. (Microprobe, 20W, 0.4  $\mu$ a, 13 min.).
- Fig. 11: (A) Dolomitized limestone section transmitted light (X50);  
(B) Cathodoluminescence of specimen 11A. Calcite is blue, dolomite, red (ELM 2A Luminoscope, 18KV, 0.1 mA, 24 sec., X50).



FIGURE 4



FIGURE 5

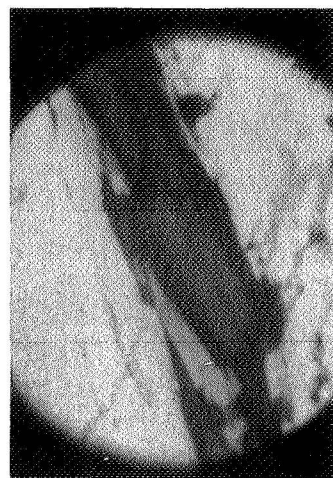


FIGURE 6

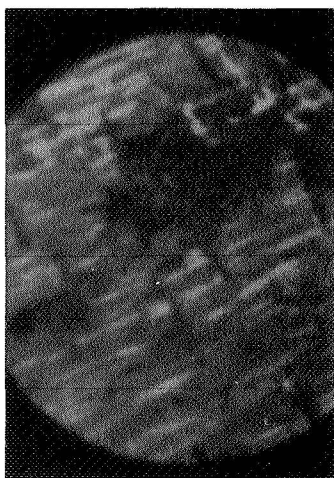


FIGURE 7



FIGURE 8

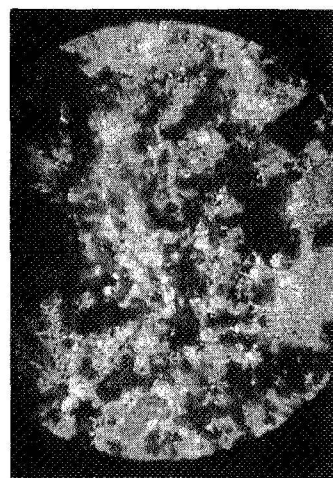


FIGURE 9

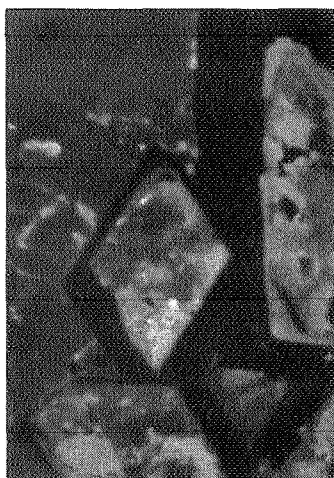


FIGURE 10

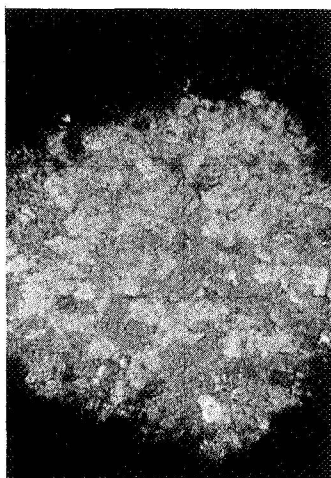


FIGURE 11A

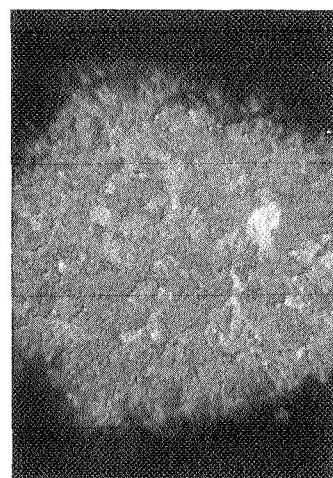


FIGURE 11B

revealed that at the center of each such area there was zirconium---a zircon crystal with radioactive thorium as impurity, the alpha-bombardment causing here a luminescence halo comparable to the "pleochroic haloes" observed when biotite mica is observed in thin sections using ordinary light.

### Feldspars

Most feldspars luminesce in the blue, with a minority showing reddish hues. Cathodoluminescence makes it possible to differentiate between sodium-rich and potassium-rich phases of a perthitic intergrowth---although to do so one must determine for each specimen which luminescence belongs to each phase.

Fig. 6 shows the cathodoluminescence of a microcline perthite from Finland. It shows a sodium-rich albite vein (dark blue) in a potassium-rich microcline host (light blue). The luminescence of the albite veins is ordinarily not uniform---there are strips of different luminescence, and ordinarily a dark rim. The secondary x-rays (studied using the microprobe) showed that the entire vein was very close in composition to pure albite, but that the more brightly luminescing strips contained more potassium and calcium. Generally there was more than 98% sodium with about 1% each K and Ca, but some specimens contained as much as 5% Ca. Several possible interpretations of these differences were proposed by Smith, including temperature of formation (the brighter center representing the beginning of ex-solution) or diffusive exchange of Na and K, or the crossing of the temperature for the microcline-orthoclase inversion.

Fig. 7 shows another perthite, from a small biotite-granite near Oslo, Norway. In this case the dark blue luminescence is from the K-rich phase and the pink and red from albite. The albite, studied by microprobe, contains essentially no Ca or K. The cause of the irregular red region is as yet unknown.

### Hematite

Fig. 8 shows a hexagonal crystal of hematite that luminesces red, surrounded by feldspar, which luminesces blue. The feldspar is aventurine from southern Norway. Note that the feldspar around the hematite has been "bleached".

### Carbonates

Some carbonates luminesce in the orange due to substitution of divalent manganese. However, transition metals (in natural samples, iron, principally) quench this luminescence.

In sandstones and shales, calcite cement is readily detectable by its orange-red luminescence, permitting one to obtain an immediate knowledge of its distribution much more rapidly than can be done by conventional microscopy. Fig. 9, a calcitic siltstone, illustrates this application.

Luminescence has proven its value in the study of calcitic rocks that have undergone dolomitization. Zoning of the dolomite rhombs is readily seen when present, and as Fig. 10 shows, iron-rich rims not seen easily in unpolarized light are obvious by their lack of luminescence (see also Fig. 4). By combining reconnaissance studies by luminescence microscopy with element mapping of local areas by microprobe analysis, Smith deduced that dolomite grows most easily from calcite containing substituted iron.

Fig. 11A and 11B illustrate the contrast in appearance of a thin section of a different specimen of dolomitized limestone when viewed in ordinary light and under electron bombardment in the Luminoscope. Here the magnification is 50X. The first slide of the pair, made with transmitted light, is not very informative. The second slide shows the luminescence: the blue areas are calcite, and the red, dolomite. The very bright blue area is possibly a calcite crystal. The usefulness of the technique in obtaining very quickly a comprehensive impression of the extent and distribution of dolomitization is apparent. And the exposure time for the Luminoscope slide was 24 seconds compared to 15 minutes for the microprobe dolomite luminescence photo discussed above.

Details of specimen history not obvious in unpolarized light or under crossed-nicols are often revealed by luminescence microscopy. Fig. 12A shows a thin section of a marble in ordinary light. Some additional information is given through using polarized light, as Fig. 12B shows. But neither technique reveals the growth history that becomes immediately obvious under electron bombardment--as is shown by Fig. 12C.

A rather spectacular example of the same effect is shown in Fig. 13--a fracture filling in a dolomitic carbonatite. In this case the contrast between the appearance of the specimen studied by luminescence and by classical microscopy is equally marked.

If the rock as originally formed contained fossils, electron luminescence will often reveal this. Fig. 14A shows a sample in plain light. But luminescence (14B) reveals that this was a shell deposit--a shell edge appears here as blue bands in the orange calcite. Magnification for this pair of slides is 50X and exposure time was 12 seconds. At lower magnifications,

Fig. 12:(A) Marble thin-section, transmitted light (X50).  
(B) Same as 12A, viewed through crossed nicols (X50).  
(C) Cathodoluminescence of same areas as in 12A and 12B, illustrating how impurities show growth history of specimen (ELM-1 Luminoscope, X50).

Fig. 13. Cathodoluminescence of fracture filling in dolomite carbonatite (ELM-1 Luminoscope X50).

Fig. 14:(A) Recrystallized limestone thin section, transmitted light (X50).  
(B) Cathodoluminescence of specimen 14A showing former presence of shells (blue). (ELM 2A Luminoscope, 18KV, 0.1 mA, 8 sec., X50).

Fig. 15:(A) Equilibrated chondrite Ausson, thin section.  
(B) Cathodoluminescence of 15A.

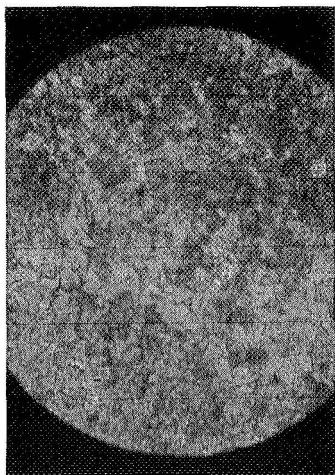


FIGURE 12A

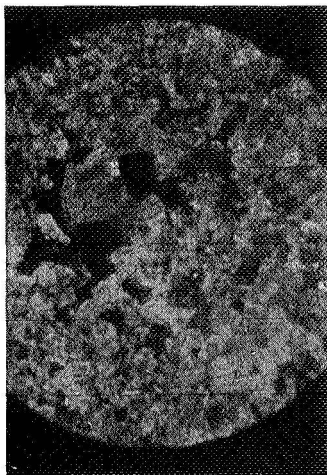


FIGURE 12B

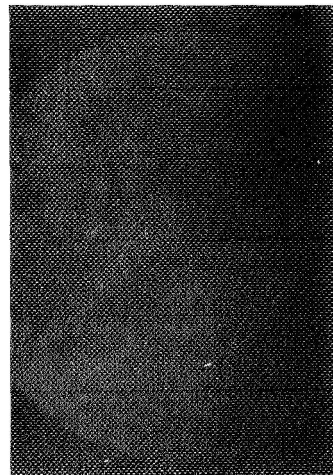


FIGURE 12C

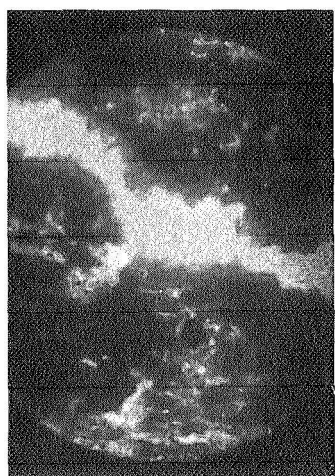


FIGURE 13

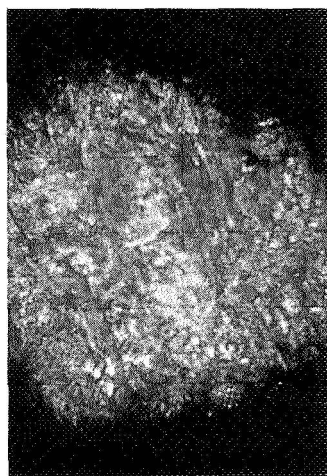


FIGURE 14A



FIGURE 14B



FIGURE 15A

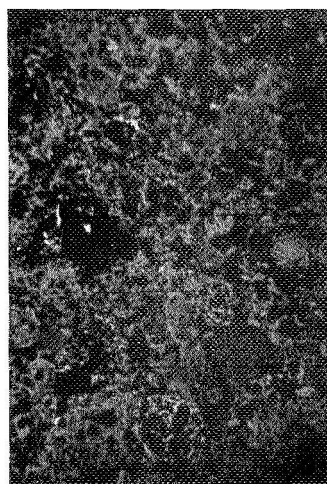


FIGURE 15B



entire shell cross-sections are clearly revealed, often making possible the identification of the shell and the assignment of the rock to a particular geological time period.

### Serpentines

The luminescence of the serpentines was studied by Weber, Greer, and Vand (1967) using 30 and 50 KeV electrons and restricting the observations to an attempt to find relationships between fluorescence spectral data and composition by microprobe studies of element distribution. Quantitative spectrochemical analyses of bulk samples for Fe, Mn, Ni, Ti and Cr were also made, the microprobe being used for Fe, Mn, Cr, Ni, and Ti. X-ray diffraction data were used to place the serpentines in subclasses in terms of the three polymorphs, crysotile, lizardite and antigorite. (Many specimens were found to be mixtures of two polymorphs.) Some grains exhibited no fluorescence, others fluoresced to varying degrees, in the orange and especially in the blue. However, no obvious relationship between either polymorph type or chemical composition, and luminescence, was found, except that iron inhibited luminescence, and whenever a sample containing appreciable Fe did fluoresce, it also had relatively high contents of Mn, Cr and Ni.

### Equilibration of Chondritic Meteorites

Wood (1969) used the Luminoscope to study equilibrated and unequilibrated chondrites. A section of an equilibrated chondrite (the meteorite Ausson) is shown in the next pair of plates, the first of which (Fig. 15A) shows the meteorite in ordinary light, the second (15B) by luminescence. There is little luminescence except in the blue; this is presumably feldspar.

The second example is the Chaipur meteorite, an ordinary chondrite. It is relatively unequilibrated. Fig. 16A is the transmitted light appearance, whereas luminescence is shown in 16B. In this case there is a rich variety of color. The orange is olivine, the pink rims are pyroxene, and the blue luminescence is, again, presumably mostly due to feldspars.

It was concluded that unequilibrated chondrites show much more luminescence than equilibrated ones, and that a criterion for determining extent of equilibration might be developed on the basis of observations of luminescence.

### Lunar Rocks

The electron-stimulated luminescence of certain Apollo 11 samples has been studied by Sippel and Spencer (1970). In these crystalline rocks and breccias, calcic plagioclase is the most abundant luminescent mineral, but luminescing

trace K-feldspar and minor cristobalite and tridymite, and possibly quartz, were also observed.

The study of the spectra of the luminescent plagioclases revealed interesting effects. In both of the specimens Sippel studied, plagioclase had an abundance of about 25 percent, while cristobalite was present at the one percent level and tridymite much less. The dominant mineral was pyroxene (about 45 percent) and there was usually about 5% olivine as well as some unidentified Fe-bearing trace minerals, which did not luminesce. Apatite and zircon, which are brightly luminescent in terrestrial rocks, were not found.

The plagioclase luminescence was blue to yellowish blue and covered a wide range of intensity as well as color. The central regions of laths, which were the brightest, proved to be calcium-rich.

Terrestrial plagioclase spectra in general are characterized by three peaks, in the blue, green, and red. In the lunar samples (100 grains having been studied) the red-infrared peak is absent completely. The reason is presently not known. Grains of "maskelynite"--that is, of plagioclase disordered by shock waves, had a different spectrum, resulting in a dull red color. Some single grains graded from this spectrum at one end to the un-shocked spectra at the other. There was evidence (supported by crossed-nicol observations) of disordering on the micrometer (micron) scale.

#### OTHER APPLICATIONS

We have concentrated in this paper on the applications of this new technique to petrology and related fields. However, there are numerous other areas of application, present and potential.

##### Production Control of Synthetic Minerals

An application area for electron luminescence microscopy that is especially closely related to mineralogy is the study of synthetic minerals. One particularly useful application is illustrated by Fig. 17, which shows the surface of a synthetic ruby crystal grown for use as a laser, sliced perpendicular to the axis. Fig. 17A was made at X20 magnification, using light transmitted through the 1/4" thick specimen. Some impurities and pits can be seen in this. But cathodoluminescence (Fig. 17B) also shows very clearly a concentric circular pattern of color variation which is certainly related to the growth history of the crystal, and, presumably, shows how this influenced the incorporation of impurities. The possibility of using the technique for quality control is obvious.

- Fig. 16: (A) Unequilibrated chondrite Chairpur, thin section.  
(B) Cathodoluminescence of 16A, showing olivine (orange), pyroxene (pink rims); note contrast to appearance of equilibrated chondrite, 15B.
- Fig. 17: (A) Synthetic ruby, 1/4" slice of rod, transmitted light (X20).  
(B) Cathodoluminescence of 17A, with "growth rings" showing impurity distribution. (ELM 2A Luminoscope, 18KV, 0.1 mA, X20).
- Fig. 18. Cathodoluminescence of synthetic strontium aluminate doped with Mn; green areas contain  $Mn^{+2}$  and red regions  $Mn^{+4}$  oxidized to  $Mn^{4+}$ . (ELM 2A Luminoscope, 15KV, 0.1 mA, 8 sec., X20).
- Fig. 19. Cathodoluminescence of irregular chunk of synthetic silicon carbide. Note growth banding. (ELM 2A Luminoscope, 0.1 mA, 0.5 sec. exposure.)

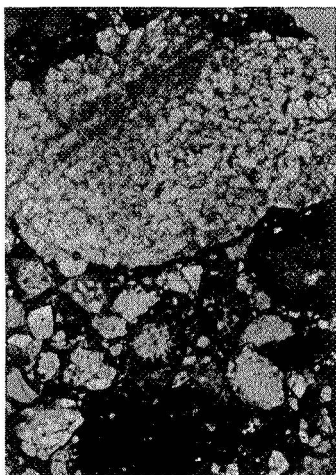


FIGURE 16A

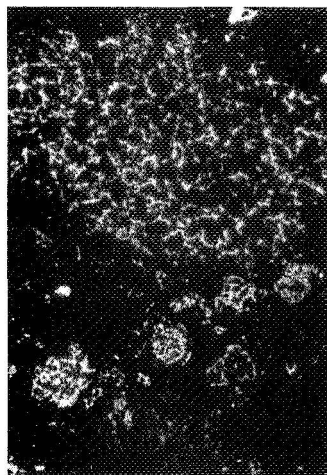


FIGURE 16B

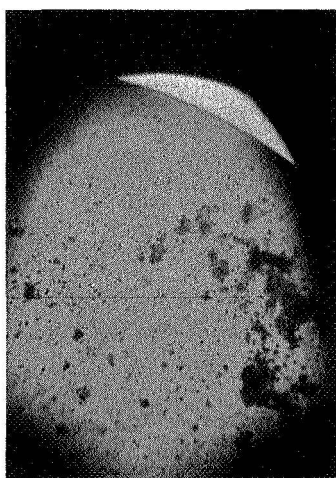


FIGURE 17A



FIGURE 17B

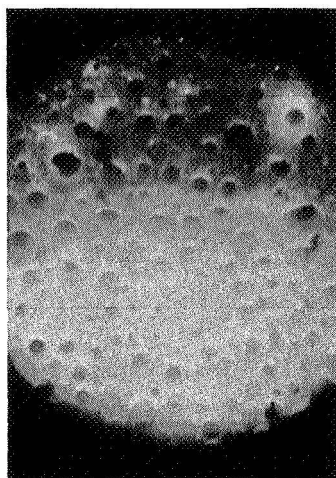


FIGURE 18

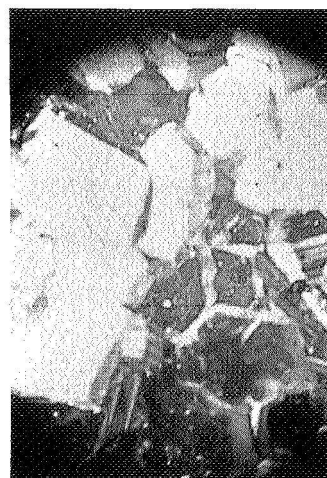


FIGURE 19

Fig. 18 (magnification, 20X) shows the cathodoluminescence of a cut-off end of a synthetic crystal of strontium aluminate, flame-grown by Bergstein (1970). The sample has been cut perpendicular to the c-axis, and only a portion is shown in the plate. The portion luminescing green is towards the center of the rod, the reddish region toward the outside. The specimen was doped with manganese and the colors are attributed to  $\text{Mn}^{2+}$  (green) where the flame was reducing and  $\text{Mn}^{4+}$  (red) where conditions were oxidizing. For this picture a Mamiya-Sekor 35mm SLR camera was used loaded with Kodak Ektachrome High Speed Type B film (125ASA, 3200°K). The specimen was bombarded with 15KV electrons, the total current being 100 microamps with approximately 10  $\mu\text{a}$  reaching the specimen; exposure time was 8 seconds.

Silicon carbide is another synthetic material that luminesces strongly, often giving a beautiful display of greens, yellows and browns (Fig. 19). This shows the surface of an irregular chunk of silicon carbide crystals at X20 magnification, luminescing under the electron beam. Structural details such as zoning during growth are clearly revealed. One occasionally encounters, in color photography of luminescence, a region which luminesces in a wave-length region to which the film has no response, and which therefore does not appear (i.e. shows up black) on the slide. Black and white film on the other hand responds to all visible wavelengths and will show this region as luminescing.

#### Other Applications

Some of the other purposes to which Luminoscopes have been applied thus far include the following: studies of human teeth (using trace elements) characterization of gem stones, quality control of special glass, and, recently, research in cultural anthropology, in particular, in attempting to assign pottery specimens to particular sources. Undoubtedly, many more applications await discovery and exploration. Electron luminescence microscopy is a powerful technique whose potential as yet remains largely unexplored.

#### ACKNOWLEDGMENTS

We would like to acknowledge the assistance of our former colleague, Dr. Robert Buchanan, in the development of the prototype Luminoscope, and of Prof. J. V. Smith for the concept, for making many useful contributions to the development of the Luminoscope, and for furnishing electron microprobe photos of luminescence. The kind cooperation of John Wood in furnishing Luminoscope slides of chondrite luminescence is also acknowledged.

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LABORATORY STUDIES OF LUMINESCENCE OF ROCKS  
AND OF NATURAL AND SYNTHETIC INORGANIC MATERIALS

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INTRODUCTION

In this paper, two methods for investigating the luminescence of various inorganic materials are proposed. Luminescence can be studied even if the luminescent matter is mixed with non-luminescent material of weak albedo. The two methods are: (1) measurements of Fraunhofer line depth, and (2) measurement of excess light superimposed upon a continuous spectrum background. Details of the Fraunhofer line depth method have been published by Dubois (1959). Luminescence has been detected for several rocks using this method. We have proved that light absorption of inactive and thin substances can distort luminescence bands. Rocks are often very absorbent in some spectral bands, but short wavelength radiation can penetrate for some distance and excite luminescence.

MATERIALS STUDIED

Natural materials

Natural rocks and minerals studied include: (1) willemite, pure; (2) willemite, impure, containing iron oxide which quenches luminescence; (3) volcanic ash from Puy de Dome, France; (4) mixture of the three above materials; (5) talc and kaolinite; (6) opal, pure; (7) ultramarine; (8) granite; (9) diorite; (10) trachyte; (11) gneiss; (12) basalt. The rocks (8 to 12) are slightly luminescent, especially if freshly broken or crushed. It appears that rock alteration caused by moist air can greatly reduce luminescence.

Synthetic materials

(13) synthetic willemite; (14) halophosphate; (15)  $\text{Fe}_2\text{O}_3$ . The first two compounds luminesce very strongly if irradiated by UV light at  $2537\text{\AA}$ , but the iron oxide is non-luminescent.

## LABORATORY METHODS

Luminescence is excited by a mercury vapor lamp emitting intense radiation at  $2537\overset{\circ}{\text{\AA}}$ . A surface at a distance of one foot from the lamp receives about the same energy at  $2537 \pm 125\overset{\circ}{\text{\AA}}$  as would the same surface receive from the sun when outside of the earth's atmosphere. On the moon, of course, the surface would also receive x-rays and corpuscular radiation. Thus, on the moon, excitation would be stronger and more extensive in wavelength than in the laboratory, and hence, luminescence would surely be enhanced.

## RESULTS

The igneous rocks we have studied are all slightly luminescent in UV light (Dubois, 1960). Most of the luminescence is localized in the long wavelength portion of the visible spectrum. We have studied terrestrial non-luminescent rocks in order to simulate processes occurring on the moon. These rocks are pulverized, then mixed with a given percentage of luminescent materials whose luminescence spectra are well known. Diffuse reflection factors of these materials are also known, the luminance of a given substance being compared with the luminance of a flat magnesia block illuminated by the sun or a UV lamp.

The results are shown in Fig. 1. The intensity unit is the one diffused by the magnesia block around  $5500\overset{\circ}{\text{\AA}}$ , illuminated either by the sun or by an incandescent lamp. Curves a and a' are the luminescence bands of materials no. 1 and 4 respectively. Curves b and c are the intensities reflected by these same two substances respectively. Curves d and e refer to the same materials but, in this case, irradiation is at  $2537\overset{\circ}{\text{\AA}}$ . A weak maximum around  $5200\overset{\circ}{\text{\AA}}$  is found on curve e, consistent with that of willemite. Curve f is that of the scattered light by substance no. 2. Note the strong maximum at  $6100\overset{\circ}{\text{\AA}}$ .

In Fig. 1, it can be seen that substance no. 2 does not entirely cancel the luminescence of the no. 4 mixture, but it does diminish it greatly and distorts the band. The maximum is clearly depressed and shifted about  $200\overset{\circ}{\text{\AA}}$  toward the red with respect to the wavelength of the luminescence maximum of willemite.

Thus non-luminescent materials when mixed with luminescent substances will disturb and shift the emission band due to absorption.



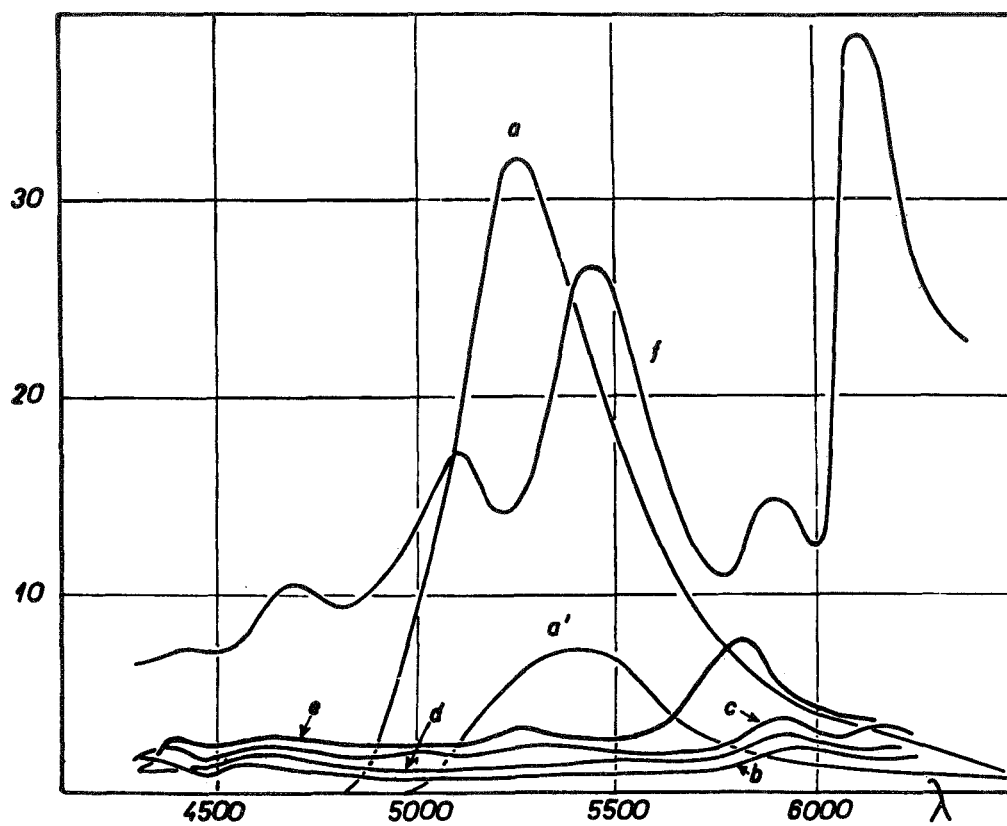


Fig. 1.

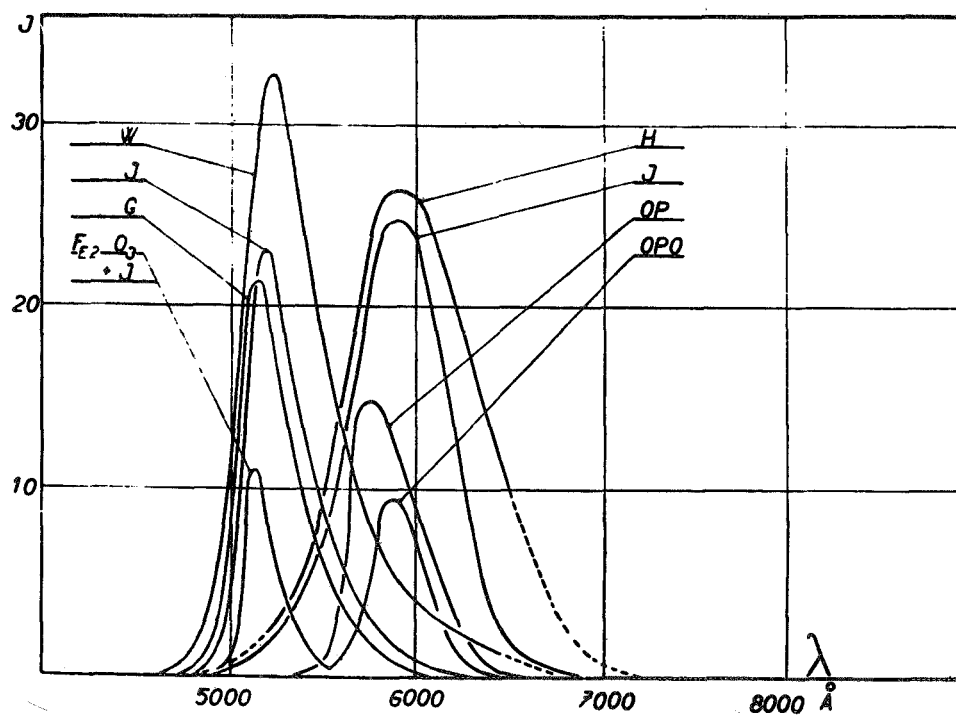


Fig. 2.

Radiation at  $2537\text{\AA}$  excites strong luminescence in synthetic willemite and "SAFPE 16-874" halophosphate. The luminescence, emitted in the visible portion of the spectrum, can be focused on the slit of a spectrograph after passing through a thin strip absorbing filter. These filters are made from glycol-water colloidal suspensions of very finely powdered non-luminescent materials. The suspension is squeezed between two thin glass plates, making a translucent, rather than transparent, filter. The following strips have been made: J-yellowish filter, mixture of equal parts of opal and substance no. 2; OP-pure opal; G-greyish strip, mixture of the "J" material and one part of ultramarine; OPO-like OP but with ultramarine added;  $\text{Fe}_2\text{O}_3$ -colloidal suspension of iron oxide;  $\text{Fe}_2\text{O}_3 + \text{J}$ -combination of filters  $\text{Fe}_2\text{O}_3$  and J.

### RESULTS

The effects of absorption on luminescence bands are shown in Fig. 2. Curves W and H are luminescence bands of pure willemite and halophosphate. Other curves show effects of light filtering by the strips. Curves J, G, and  $\text{Fe}_2\text{O}_3 + \text{J}$  are obtained from the luminescent light of willemite filtered by the strips J, G, and  $\text{Fe}_2\text{O}_3 + \text{J}$  respectively. Curves J, OP, and OPO are the curves for the luminescence of halophosphate filtered by the appropriate filter strips.

An important feature of Fig. 2 is the decrease in the intensity of luminescence accompanied by band narrowing. The degree of narrowing is greater than that which could be obtained by multiplying the ordinates of the W and H curves by a factor less than one. The wavelength shift of the maximum is shown in the following table:

Filter-strip	Luminescent matter	Maximum shift (in $\text{\AA}$ )	Band narrowing (in percent of the breadth of luminescent substance bands)
J	willemite	50	12
G		100	19
$\text{Fe}_2\text{O}_3$		100	60
J	halophosphate	0	25
OP		200	55
OPO		0	65

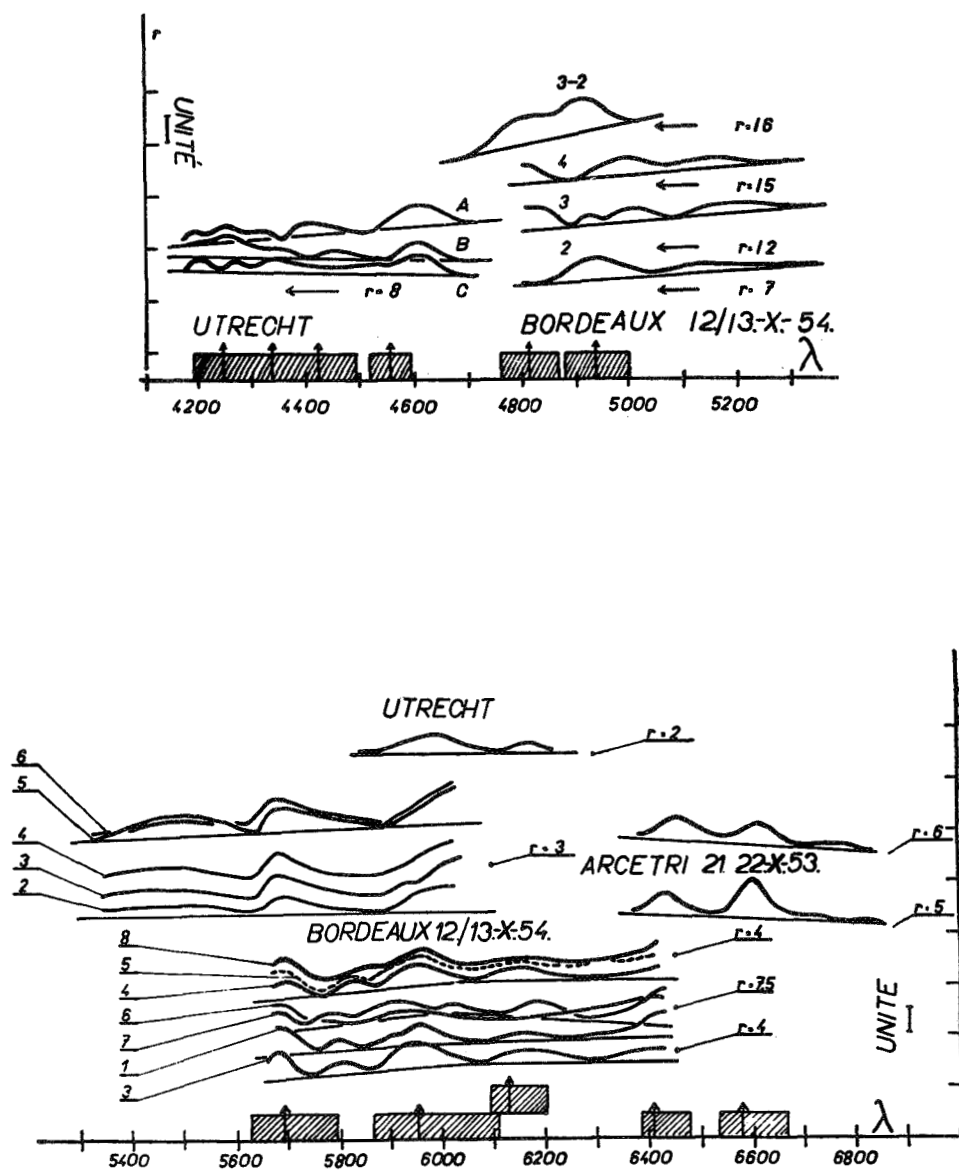


Fig. 3.

We conclude that silicates or oxides can greatly modify the appearance of a luminescence band. The narrow bands observed on lunar spectra may result by the "cutting up" of a broad luminescence band by absorption.

#### REMARKS

We can also detect luminescence by measurements of the increase in intensity of the light scattered by the moon, comparing luminescent and non-luminescent regions of the moon. Assuming luminescence does exist, the light scattered by the moon, plotted versus wavelength, provides a curve with one or several maxima, at the place where luminescence bands have been confirmed by Fraunhofer line depth measurements. The luminescence bands derived from the excess of light over continuous background are shown in Fig. 3. No.'s 1 to 8 indicate lunar regions; horizontal arrows show the position of number units given by  $r$ , where  $r$  is the ratio  $B/B_0$ .  $B$  and  $B_0$  are the luminance of the moon and of a magnesia block respectively.

If the albedo of the materials is weak, as on the moon (about 0.07), the intensity of luminescence can be measured even if the percentage of luminescent minerals in the material is less than 0.3 or 0.4%. But for such cases it is necessary to use the Fraunhofer line depth method. If the albedo exceeds 0.5, the minimum concentration of luminescent minerals must be greater than 1% in order to detect luminescence.

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## EXISTENCE AND STUDY OF LUNAR LUMINESCENCE

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## INTRODUCTION

The existence of lunar luminescence has been proposed by Link (1946) to explain the excess of light observed in penumbra during eclipses of the moon. Light scattering in the terrestrial atmosphere, or variations in its transparency cannot account for large changes of luminance when the moon is eclipsed. New investigations of a great many photometric observations of lunar eclipses corroborate this conclusion.

Lunar luminescence can be excited by solar radiation. Support for our hypothesis may be found in significant correlations between luminous variations of the moon and solar radiance (Link, 1947; 1949; 1950; 1956). Direct verification of lunar luminescence, however, is desirable. This was undertaken by studying Fraunhofer line depth variations (Dubois, 1959), by comparison of a solar and lunar spectrum.

If the lunar surface is composed of the same sort of igneous rocks found on earth, lunar luminescence could be a real phenomenon (Dubois, 1960). Although there may be differences in the physical structure of lunar and terrestrial rocks, the constituent minerals are likely to be similar. Many crystalline terrestrial rocks are more or less luminescent. On the moon, of course, luminescence will be enhanced because of the greater range in wavelength and much greater intensity of the exciting radiation than are used in our laboratories.

Greenman and Gross (1970) have studied the luminescence of lunar samples from the Apollo 11 landing area (Mare Tranquillitatis), and also the luminescence of some terrestrial rocks and minerals. In their experiments, the minerals were excited by UV radiation around  $3000 \text{ \AA}$ , and the luminescence was found to be very weak. Perhaps it would be necessary to irradiate the materials with a very large UV spectral band, rather than with a single radiation or a narrow band.

## DIRECT STUDY OF LUNAR LUMINESCENCE

The study of lunar luminescence can be undertaken in several different ways. Cimino and Fortini (1953) and Cimino and Fresa (1958) compared the luminance of some lunar regions in general spectral bands when the moon was eclipsed. Some regions studied were luminescent, but others were not.

The Fraunhofer line depth method is a very general one, but it is both accurate and sensitive. In Fig. 1,  $H_{\beta}$  is an absorption line of the solar spectrum. Assume that a given area of the moon is luminescent in this spectral band when it is irradiated by short wavelength radiation. Let the excess light caused by luminescence be equal to 1% of the scattered intensity around the  $H_{\beta}$  line due to the lunar surface, i.e., 1% of the background lunar spectrum. Referred to the center of the dark  $H_{\beta}$  line, this quantity 1% becomes much more important. If the luminescence in the center of the  $H_{\beta}$  line is 1/20 of the background around the line wings, this level of luminescence will amount to about 20% of the intensity in the center of this line. That is, the  $H_{\beta}$  line will appear less deep than it would if luminescence were not occurring. The line is thus distorted and a study of this distortion provides an indication of the intensity of the luminescence.

Let:  $I$  = the background intensity around the line wavelength;  $i$  = the intensity at the center of the line;  $R = i/I$ , the line depth ratio;  $i_f$  = the supplementary intensity related to luminescence;  $p$  = the factor of reflection of the material which scatters solar light. According to Dubois (1959), the decrease in line depth is:

$$\Delta R = i_f \frac{1-R}{pI + i_f}$$

If  $R$  is obtained from the solar spectrum and  $R'$  from the lunar spectrum,

$$\Delta R = R' - R$$

$I$  can be measured by studying the lunar spectral background. The value of  $p$  ranges between 0.1 and 0.2. Thus,

$$\rho = \frac{i_f}{pI}$$

The value of  $\rho$  is expressed in percent, and it gives the intensity of the luminescence. The accuracy in determining  $\rho$  has been discussed by Dubois (1959). If a deep line is chosen ( $R$  about 10%), the relative error is 2%.

Our observations have shown that  $\rho$  can be measured provided its value is greater than 2%. Below 2%, accuracy in determining  $\rho$  greatly decreases and the occurrence of luminescence is conjectural. An area on the moon is

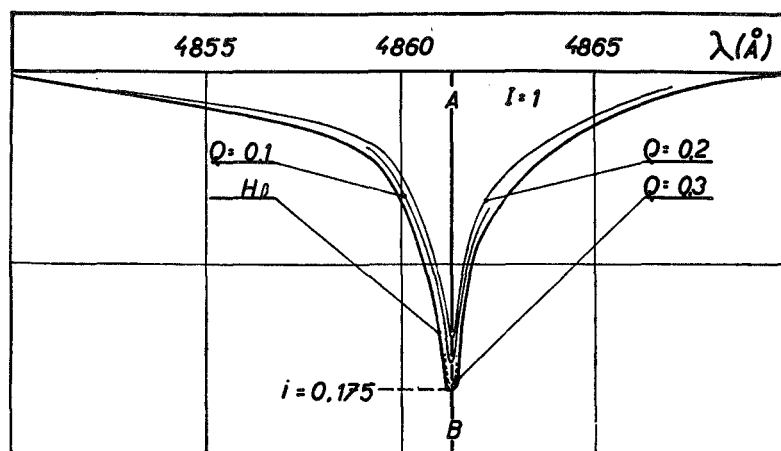


Fig. 1.

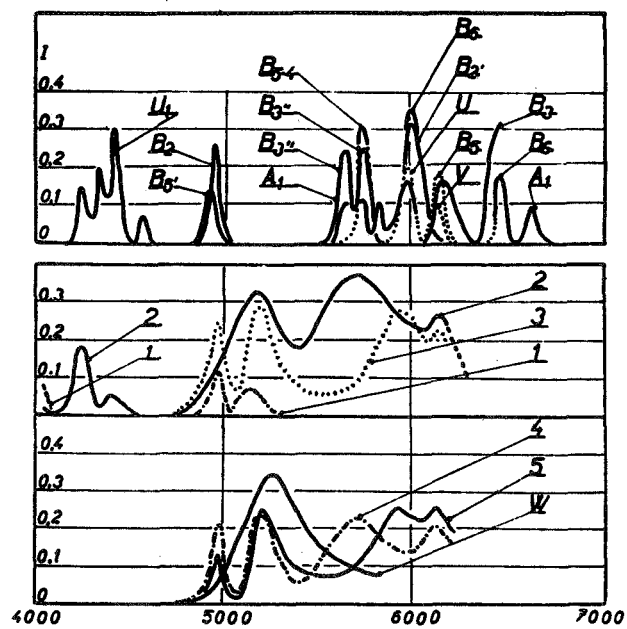


Fig. 2.

considered to be luminescent if at least three measurements of  $\rho$  have indicated luminescence with a value of  $\rho$  greater than 2%.

## RESULTS

All of the lunar and solar spectra to be compared have been obtained with the same spectrograph. Large dispersion is necessary, at least 15 to 20 Å/mm in the green. Either prisms or a grating can be used. We have attempted measurements with smaller dispersions, but these are useful only if the luminescence is very intense. The spectra studied have been obtained using three types of spectrograph at Bordeaux, and from the solar tower spectrograph at Arcetri (Italy). Other spectra were recorded by Van t' Veer, at Utrecht, using a prism spectrograph for the blue and green regions, and a grating spectrograph for the red.

The spectra analyzed are shown in Fig. 2, where A, B, and U represent data obtained from Arcetri, Bordeaux, and Utrecht respectively.  $B_2$  and  $B'_2$  are the bands referred to a dark region between Mare Nubium and Mare Humorum.  $B_3$  and  $B''_3$  are the bands for a bright region between Mare Vaporum and Mare Nubium.  $B_4$  refers to Sinus Medii - Mare Vaporum.  $B_5$  is from a bright area between Mare Vaporum and Mare Serenitatis.  $B_6$  is from the center of Mare Serenitatis. 1 refers to an adjacent region between the western edge of the moon and Mare Crisium; 2 indicates the center of Mare Crisium; 3 - the western part of Mare Frigoris; 4 - a region between Aristote Circus and the center of Palus Nebularum. W refers to the band from synthetic willemite.

We have studied 86 regions of the moon. On the schematic map in Fig. 3, 27 areas are shown where luminescence has been detected. The hatched lines designate zones in which luminescence has not been found. Question marks are used to show regions in which luminescence is probable but for which we have not yet been able to obtain the three consistent observations necessary to assure luminescence by our definition.

Identification of luminescence bands - If luminescence is highly specific, it is desirable to attempt to determine what materials might be found on the lunar surface, using these bands for determination. This task is very difficult. Several bands, for example, are very narrow, and it is difficult to ascribe them to a particular material. Our colleague, Mr. Servigne, believes that an absorption phenomenon superimposed on the luminescence emission band could explain the observed blue to green bands. In the green region, the bands could be due to the natural zinc orthosilicate, willemite. This mineral is





abundant in some areas on earth (Dubois, 1956). The yellow to orange bands could also arise from willemite if small amounts (0.1-0.2%) of manganese are present. The yellow band itself could be attributed to various silicates.

#### LUNAR LUMINESCENCE STUDY FROM LIGHT CURVES OF THE ECLIPSED MOON

This method is an indirect one. When the moon is in penumbra (at the beginning or the end of an eclipse of the moon), a portion of the sun's rays coming from its disc are hidden by the earth. However, radiation from certain active centers of the sun, as well as from the chromosphere and corona, may still strike the moon. The lunar surface is much less illuminated by the photosphere, and hence receives visible light of low intensity. The moon can, however, receive very powerful UV, X, or corpuscular radiation capable of exciting luminescence on the lunar surface.

The geographic and heliographic details of the eclipses have been described by Dubois and Link (1969) and the cat-eye photometer by Dubois (1942). The photometer measurements are free of variations in atmospheric transparency. Clouds, if not too dense, do not interfere with the measurements.

Let  $\gamma''$  represent the distance of an observed point from the geometric edge of the umbra. If  $\gamma''$  is between 0 and 25 minutes of arc, we can compare the observed density of the penumbra with its computed value. The choice of  $\gamma''$  is fully justified, as this distance is practically independent of parallax of the moon, principally into the inner penumbra. Comparison of the observed excess light with the theoretical values is made in Fig. 4 for 21 eclipses between the years 1922 and 1968. This figure shows the density of the penumbra (expressed in magnitudes) for several values of  $\gamma''$  between 0 and 25' from the edge of the umbra. Each determination is represented by an empty square for the increasing phase. Those containing an asterisk pertain to the decreasing phase. Arrows indicate the computed density. Fig. 4 shows that when  $\gamma'' < 15'$ , an excess really exists. This disappears when  $\gamma'' = 15'$ . When  $\gamma'' > 15'$ , it appears as a light defect in the outer penumbra.

The results shown in Fig. 4 can be accounted for by the existence of a luminescent component in the light received from the moon during an eclipse. This component most likely arises from excitation by radiation from the solar corona and chromosphere, as well as radiation from the sun's active regions.

Let the unit be the total light from the moon. Let  $\ell$  be the portion of the light due to luminescence. The photospheric light scattered by the lunar surface is  $I - \ell$ . Let  $e$  represent the fraction of the photosphere not hidden

by the earth, and  $\varepsilon$  that of the area where the excitation is coming from.

The observed luminescence will be:

$$O = (I - l) e + l\varepsilon \quad .$$

The difference between an observed and computed value is:

$$O - C = l(\varepsilon - e) \quad .$$

The values of  $l$  are obtained from theory (Link, 1956). In the case of the solar corona,  $\varepsilon$  is obtained from:

$$\varepsilon_1 = \frac{4}{360} \quad ,$$

and for active zones:

$$\varepsilon_2 = \frac{X}{X_0} \quad .$$

These notations are clarified in Fig. 5, where variations in  $O-C$  are shown as a function of  $\gamma''$  for the case of the corona (c) and the case of two active zones (Z).

In Fig. 5, the corona and the active zones are the sources of excitation. If the source is a rather large  $K_3$  area of ionized calcium, we could observe a disturbance of the  $O-C$  curve when the solar area passes over the edge of the earth. If both sources of excitation are considered, it appears that the Z curve of Fig. 5 agrees quantitatively better with reality, as the  $O-C$  difference is smaller if  $\gamma'' < 15'$  than if  $\gamma'' > 15'$ . According to recent pictures of the sun in the UV-X regions, obtained from rocket flights, the sources of these exciting radiations are located above the  $K_3$  areas, visible on the spectroheliograms.

For each eclipse, we have drawn the view of the partial solar eclipse as seen from a measured point of the penumbra. These are for earth positions corresponding to  $\gamma''$  distances equal to  $0'$ ,  $5'$ , and  $10'$ . The drawings have been superimposed upon the  $K_3$  spectroheliograms in Fig. 6.

In Table 1, comparison is made between solar situations and observed effects in the penumbra. The individual influence of the  $K_3$  areas and of the activity zones is shown.

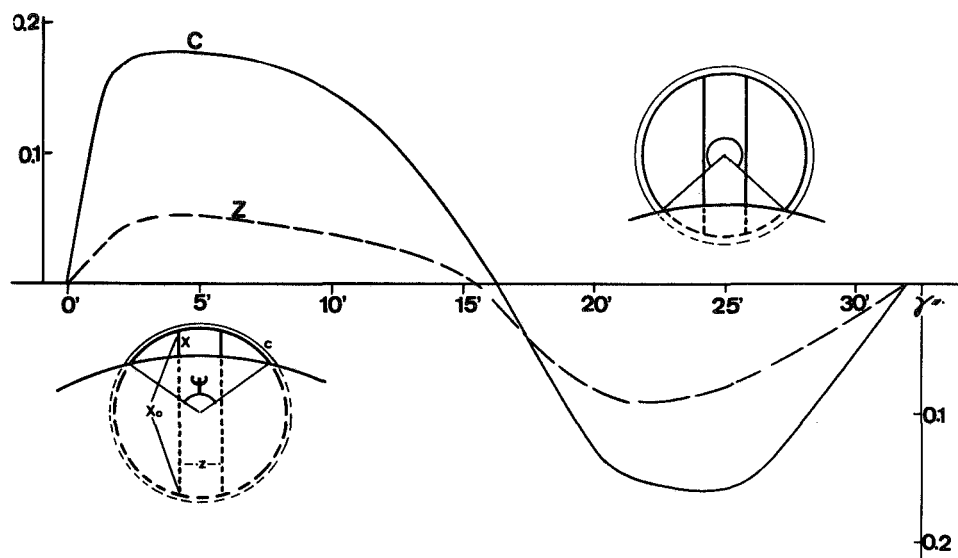


Fig. 5.

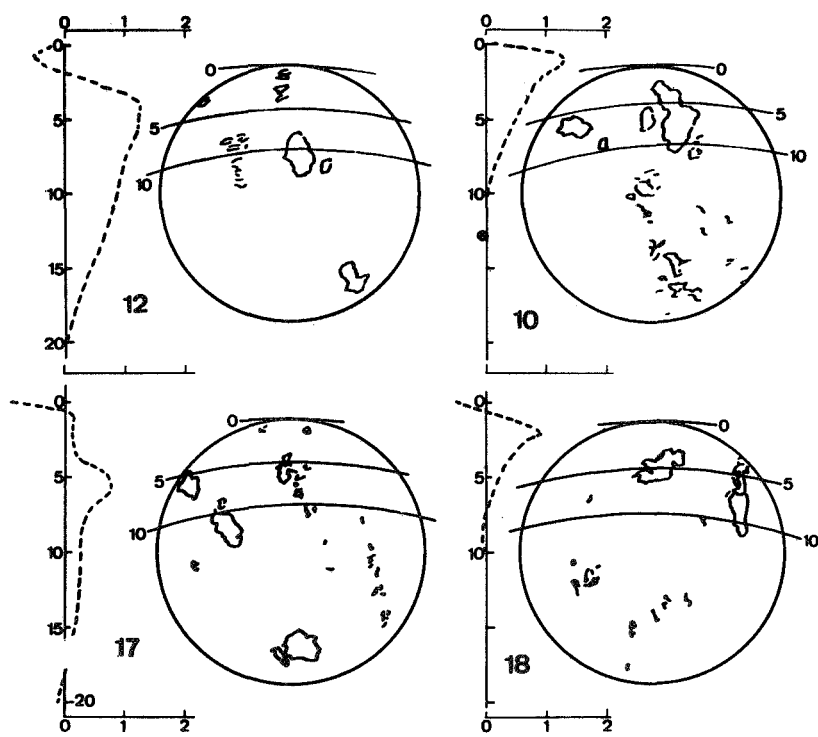


Fig. 6.

TABLE 1

Nr.	Date	Sun	Penumbra	Remarks
5	1942-VIII-26	Intense area at the edge	Excess near the edge	Incomplete curve
9	1946-XII- 8	Area between 2,5' and 4'	Excess between 2' and 5'	
10	1949-IV- 13	Intense area between 2' and 12'	Excess between 0' and 10'	Figure 6
12	1950-IX- 26	N. and S. zones of the areas	Excess between 2' and 20'	Figure 6
16	1954-VII- 15	Eastern part without area; Western part with one area at 7' and another at 2'	Normal curve Excess from 0' to 15'	Increasing phase Decreasing phase
17	1956-XI- 19	Two N. zones and two S. zones; areas from 0 to 15'	Excess from 2' to 15'	Figure 6
18	1957-V- 13	Some weak areas on the eastern middle; Two large and intense areas between 2,5' and 12'	Normal curve with a weak excess from 0' to 3' Excess from 3' to 15'	Increasing phase Figure 6
19	1961-VIII-26	Areas at 2' and 8' to 20' Weak N. zone	Excess from 0' to 20' Light defect	Increasing phase Decreasing phase
21	1968-IV- 13	N. and S. zones poor in areas	Excess between 2' and 10'	

Balmont and Chanon (1968) have measured the value of  $\rho$  for luminescence during the lunar day. These observers obtained a significant value for  $\rho$  from one to three days after sunrise. Subsequently,  $\rho$  decreases and becomes zero at sunset. These results suggest that direct solar radiations are not sources of excitation. It appears, rather, that the luminescence excess measured in the penumbra is due to particular sources on the sun.

Thermoluminescence does not appear to be involved, as we would systematically observe, during an eclipse, a greater excess during the increasing phase than in the decreasing phase. At this time, it is sunset for the observed point on the moon. Observations do not indicate this.

It would be desirable to measure the intensity of luminescence in the penumbra with a rather rapid method, so that changes in  $\rho$  could be observed during an eclipse, that is, under various temperature or excitation conditions. It would be necessary to measure the density of the penumbra at the same time and for the same area of the moon, in order to compute the value of  $\lambda$ .

Using Apollo 11 and 12 samples, it would be possible to reproduce the effects of an eclipse of the moon at the penumbra phase in the laboratory. The exciting radiation should be in broad UV and X bands. An experiment to study the "in situ" luminescence and thermal behaviour of the lunar surface, undisturbed by human presence, could be made in the next Apollo flight.

Attempts have been made to explain the excess light of the eclipsed moon in penumbra by an increase in atmospheric transparency or by diffusion of light by the atmospheric ring, as our atmosphere appears when it is seen from the moon. These explanations are not consistent with the order of magnitude of the excess light. For example, the atmospheric ring would have to be a thousand times more luminous than a very bright cirrus cloud.

#### CONCLUSIONS

The agreement obtained by several experimenters and methods has dispelled any doubts of the existence of lunar luminescence. Photometric measurements of the eclipsed moon not only demonstrate the lunar luminescence phenomenon but also make it possible to locate the sources of the radiation causing excitation.

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